

Detailed Investigation of Pyrolysis Mechanism of Indian Oil Shale

Thesis submitted in partial fulfilment of the
requirements for the degree of,

Doctor of Philosophy

by

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July, 2022

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STATEMENT

I do hereby declare that the content embodied in this thesis entitled “**DETAILED INVESTIGATION OF PYROLYSIS MECHANISM OF INDIAN OIL SHALE**”, is the result of investigation carried out by me at the Department of Chemical Engineering, Indian Institute of Technology Guwahati, Assam, India under the guidance and supervision of Dr. Pankaj Tiwari. In keeping with the general practice of reporting scientific observations and findings, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

Date: 20th July 2022

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CERTIFICATE

This is to certify that the thesis entitled **“DETAILED INVESTIGATION OF PYROLYSIS MECHANISM OF INDIAN OIL SHALE”**, submitted by Mr. Bhargav Baruah (Roll No. 176107004), a research scholar in the Department of Chemical Engineering, Indian Institute of Technology Guwahati, Assam, India for the award of the degree of Doctor of Philosophy is a record of an original research work carried out by him under my supervision and guidance. The Thesis has fulfilled all requirements as per the regulations of the institute and in my opinion has reached the standard needed for submission. The work documented in this thesis have not been submitted to any other university or Institute for the award of any degree.

(Dr. Pankaj Tiwari)

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Dedicated to my Parents

And

Energy Conversion Technology Laboratory



Acknowledgement

Team work, contribution, and co-operation are the most vital elements for the successful accomplishment of any task or research activity. Thereby, it is my pleasant duty to express my gratitude and heartiest thanks to one and all who were directly or indirectly involved or have contributed to my PhD work.

Foremost, I, Bhargav Baruah would like to express my sincere gratitude and thanks to my PhD supervisor, Dr. Pankaj Tiwari. It was his continuous support and guidance during my PhD, that I have been able to successfully complete my research. His immense knowledge, patience, motivation, and support have made me able to fulfil the objectives of my PhD. He has been a great mentor, a guide and a guardian during my entire PhD. His advice and guidance on my research and career have been priceless, and enabled me to groom myself as a researcher.

I am extremely grateful to my doctoral committee members, Prof. Vaibhav V. Goud, Prof. Kaustubh Mohanty from the Department of Chemical Engineering, and Dr. Archana Nair from the Department of Civil Engineering for their valuable comments and suggestions throughout my entire PhD towards the improvement of my research work.

I would like to express my sincere thanks to all the faculty members, Scientific and staff members of the Department of Chemical Engineering for their guidance, and cooperation during my course work and analytical activities during the duration of my PhD. I would like to thank the analytical laboratory at the Department of Chemical Engineering, Centre of Sustainable Polymer, and Central Instruments Facility IIT Guwahati for providing me access to different analytical instruments whenever needed during my PhD. I would also like to acknowledge the Centre of Excellence Oil India Limited for providing specific analytical facilities.

I am immensely thankful to all my laboratory members and co-researchers at Energy Conversion Technology Laboratory. I am especially thankful to my seniors Dr. Ali S. Reshad, Dr. Rahul Saha, Dr. Pallab Das, Dr. Ranjan Phukan, Dr. Poulami Datta, and Mr. Jitendra Singh Rawat for their never-ending help, support, and encouragement during my PhD. I would like to mention my lab-mates and juniors Vikas Kumar Sharma, Govind Dubey, Bibari Boro, Puja Kalita, Punampriya Borgohain, Samujjal Paul, Vishal, Sachin, Shikha Solanki, Jayant Mathur, Musaddique Ahmed, Mansi Chopra, and Killi Vikas for their support, assistance, and encouragement. I would also like to thank my friends and batchmates and seniors, Kaustubh Khaire, Pravin Suryawanshi, Shekhar Jyoti Pathak, Deepak Mishra, Ankush Sontakke, Shweta Kumbhar, Swarna Makkitaya, Naveen Yaranal, Keshav Kumar, Anasuya Talukdar, Jinesh Machale, and Rupak Bhowmik for their support and encouragement during the highs and lows of my stay at IIT Guwahati.

I would also like to express my sincere thanks to NEC Coal Fields, Coal India Limited, Margherita, Assam for providing us with the oil shale samples. I would also like to express my gratitude and thanks to my MTech supervisor Prof. Rupam Kataki, Department of Energy, Tezpur University and Mr. Parash Thakur, General Manager, Production, OIL Duliajan for their encouragement and motivation.

Finally, I would like to thank my parents and Shraiya whose blessings, guidance, encouragement and support have made this possible.

Sincerely,

Bhargav Baruah

Abstract

Pervasive requirement and utilization of reliable and readily available energy sources have led to the progressive depletion of conventional fossil fuel reserves. This has brought the unconventional fossil fuel reserves into focus. The unconventional petroleum resources are proven to hold a huge reserve around the world. One such resource is oil shale. Oil shale is a finely grained, porous, sedimentary rock which contains organic matter known as kerogen, concealed inside a mineral matrix. Kerogen is a complex organic compound which acts as the source of production of both conventional and unconventional petroleum and natural gases. On the application of heat, kerogen converts into bitumen which further breaks down into oil and gas. The most common and suitable method for production of oil and gas from oil shales as an alternative to conventional crude oil and natural gas is by retorting or pyrolysis. The total recoverable oil shale reserve around the world has been estimated to be about 3000 billion barrels of oil recoverable. United States of America has the highest reserve of oil shale estimated at 2118 billion barrels oil recoverable, followed by China (328 billion barrels oil recoverable), and Russia (271 billion barrels oil recoverable). India has a total oil shale reserve worth 15 billion barrels of oil recoverable. In India, the oil shales mostly occur among the coal seams in the Upper Assam region of North East India as outcrops. During oil shale pyrolysis process, the pyrolysis parameters significantly influence the yield and composition of the produced hydrocarbons. The mineral matters present in oil shale play a significant role in retorting or pyrolysis of oil shale. Inherent minerals such as silica, carbonate, pyrite etc. can drastically govern the heat transfer in oil shale, and influence the composition of products formed during pyrolysis of oil shale as an inherent catalyst.

The current work presents a comprehensive study on the maturation mechanism of oil shales. In the present study, the oil shale samples were procured from Tikak Colliery of Makum coal field, Upper Assam, India. The collected oil shale samples were subjected different physicochemical, compositional, petrographic and thermogravimetric analysis. The oil shale sample were found to be of siliceous type, and sour in the presence of aliphatic, aromatic and phenolic compounds. Thermogravimetric (TG) analysis of the oil shale samples showed a total organic matter content of 21 wt%. The oil shale samples were subjected to different lab-scale pyrolysis experiments in novel pyrolysis reactors. The effect of pressure on the degradation kinetics and product yield and composition was studied. The kerogen was isolated from the oil shale sample to visualize the maturation of source rocks in the sub-surface. The oil shale samples were subjected to hydrous pyrolysis experiments to replicate the maturation of source rocks into hydrocarbons by geological phenomenon. Finally, the oil shale samples were blended with lignocellulosic biomass to study the catalytic effect of inherent minerals in the oil shale during co-pyrolysis process.

Kinetic study of oil shale pyrolysis process was performed on TG data using three model-free isoconversional methods, viz. Friedman, Starink, and AIC method. The reaction mechanisms were determined using the Criado master plot. The average apparent activation energy for the pyrolysis process of oil shale and isolated kerogen showed activation energy values in the range of 216 kJ/mol to 247.54 kJ/mol. However, Under the pressurized condition, oil shale exhibited mean apparent activation energy values ranging from 341 kJ/mol to 451 kJ/mol with increase in pyrolysis pressure from 5 bar to 30bar. For the co-pyrolysis process, the mean apparent activation energy values were determined to be 249.5 kJmol⁻¹ for oil shale to rubber seed shell blend ratio of 1:2 and increased to 275 kJmol⁻¹ for blend ratio of 2:1. Lab-scale pyrolysis experiments of the oil shale samples were

performed at atmospheric pressure using RSM optimization to identify the effect of process parameters on yield and composition of product products. This study showed maximum oil yield of 12.54 wt/wt% with 9.76 wt/wt% gas yield at the optimum condition of 600°C pyrolysis temperature and heating rate of 10°C/min, for particle size of 150 micron with holding time of 2 hours. High-pressure pyrolysis of the oil shale sample showed decrease in oil yield with increase in pyrolysis pressure and increase in concentration of gases due to cracking and the occurrence of secondary reactions. The results showed that kerogen initially matures into bitumen, and thereafter, gets converted to oil and gas in the presence of inherent minerals. A few targeted Soaking and hydrous pyrolysis experiments were performed to simulate the in-situ maturation of source rocks during the catagenesis process in the sub-surface. Further, co-pyrolysis of oil shale with lignocellulosic biomass was performed to study the catalytic effect to the inherent minerals present in the oil shale. To understand the synergy of the co-pyrolysis process, the pyrolysis parameters were optimized to maximize the oil yield and simultaneously lower the concentration of the -OH compounds in the produced pyrolytic oil.

Identification of the evolved products during oil shale pyrolysis showed presence of CH₄, CO₂, aliphatic C-H, aromatic C-H and sulfur oxide functional groups. The relative concentration of C₂-C₄ gases obtained at high pressure increased dramatically compared to atmospheric pressure. The oil samples produced during pyrolysis of oil shale were found to be aliphatic in nature with carbon number distribution up to C₃₈, however, High-pressure pyrolysis showed carbon number distribution up to C₂₂. SimDist analysis showed an increase in the percentage of lighter (gasoline) and middle (kerosene) fractions from 26.2 wt/wt% and 18.3 wt/wt% at 1 bar to 45.3wt/wt % and 47.2 wt/wt% at 30 bar, respectively. The oil produced from soaking and hydrous pyrolysis showed the evolution pattern of aliphatics, aromatics, and heteroatomic compounds during the formation

of hydrocarbons in the sub-surface. Characterization of the pyrolytic oil obtained co-pyrolysis of oil shale with rubber seed shell showed that with increase in concentration of oil shale in the blend, the percentage of -OH compounds decreased in the oil samples. GC analysis of pyrolytic gases showed that with the increase in blend ratio (more oil shale), the percentage of C₃-C₅ gases increases. GC-MS analysis showed the carbon number of the produced oil samples to be in the range of C₆ to C₂₂. The aliphatic content in the pyrolytic oil increased from 19.2 % to 31.15%, and -OH percentage decreased from 41.42% to 32.1% with increase in concentration of oil shale in the blend.

This thesis develops an in-depth understanding of the thermal degradation mechanism of Indian oil shale, and present a visualization of the evolution pathway of hydrocarbons inside the source rocks in the subsurface. Detailed characterization of the pyrolytic oil produced during standard pyrolysis of the oil shale sample abundance of aliphatic compounds. The oil and gas samples obtained from high pressure pyrolysis showed high concentration of middle and light fractions, with abundance of C₂ and C₄ gaseous compounds, respectively. The pyrolytic oil samples obtained from the different types of pyrolysis processes showed the gross calorific value (GCV) to range from 23 MJ/kg to 42 MJ/kg. The presence of high energy density compounds shows that the oil shale can be used as a viable feedstock for production of high value products as an alternate to conventional crude oil and natural gas. The decrease in concentration of -OH compounds and increase in aliphatic compounds with increase in percentage of oil shale in the blend during co-pyrolysis experiments also suggests the oil shale sample as a viable feed stock with catalytic properties for co-pyrolysis with lignocellulosic biomass and other carbonaceous materials. At these conditions, the Indian oil shale possesses the potential to be an important source of high-value fuels.

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Abbreviations and nomenclatures

A	<i>Pre-exponential factor (sec^{-1})</i>
AC	<i>Ash content</i>
AIC	<i>Advanced Isoconversional</i>
ANOVA	<i>Analysis of Variance</i>
ASTM	<i>American Society for Testing and Materials</i>
ATR	<i>Attenuated transmitted reflectance</i>
C	<i>Carbon</i>
CCD	<i>Central Composite Design</i>
CHNS	<i>Carbon Hydrogen Nitrogen Sulfur (Ultimate analysis)</i>
DI	<i>De-ionised</i>
DTG	<i>Differential thermogravimetry</i>
E_a	<i>Activation energy (kJmol^{-1})</i>
EDX	<i>Energy Dispersive X-ray</i>
$f(\alpha)$	<i>Reaction mechanism</i>
FC	<i>Fixed Carbon</i>
FESEM	<i>Field Emission Scanning Electron Microscope</i>
FID	<i>Flame Ionization Detector</i>
FTIR	<i>Fourier transform infrared spectroscopy</i>
FWO	<i>Flynn Wall Ozawa</i>
$g(\alpha)$	<i>Integral form of reaction mechanism</i>
GC	<i>Gas chromatography</i>

GC-MS	<i>Gas chromatography-Mass spectrometry</i>
GCV	<i>Gross Calorific Value</i>
H	<i>Hydrogen</i>
HI	<i>Hydrogen index</i>
HP-TGA	<i>High-Pressure Thermogravimetric Analyzer</i>
k(T) or k	<i>Reaction rate constant (sec⁻¹)</i>
KAS	<i>Kissinger Akahira Sunnose</i>
MC	<i>Moisture content</i>
N	<i>Nitrogen</i>
NMR	<i>Nuclear magnetic resonance</i>
ODE	<i>Ordinary differential equation</i>
OI	<i>Oxygen index</i>
OS	<i>Oil shale</i>
P	<i>Pressure (bar)</i>
R	<i>Gas constant (8.314 Jmol⁻¹K⁻¹)</i>
RON	<i>Research octane number</i>
RSM	<i>Response Surface Methodology</i>
RSS	<i>Rubber seed shell</i>
SimDist	<i>Simulated Distillation</i>
SO	<i>Shale oil</i>
SS	<i>Stainless Steel</i>
T	<i>Absolute temperature (°C)</i>
t	<i>Conversion time (sec)</i>

TCD	<i>Thermal Conductivity Detector</i>
TGA	<i>Thermogravimetric analyser</i>
TGA-FTIR	<i>Thermogravimetry analyser-Fourier transform infrared spectroscopy</i>
TOC	<i>Total organic carbon</i>
VM	<i>Volatile matter</i>
w_0	<i>Initial weight (g)</i>
w_t	<i>Weight (g)</i>
w_T	<i>Weight at temperature, T</i>
w_α	<i>Weight at conversion, α</i>
XRD	<i>X-ray Diffraction</i>
ZSM5	<i>Zeolite socony mobil-5</i>
α	<i>Conversion degree</i>
β	<i>Heating rate ($^{\circ}\text{Cmin}^{-1}$)</i>
i	<i>Various temperature program (from 1 to n, n being the total number of temperature programs)</i>
j	<i>Suffix representation of temperature program other than i^{th} program</i>
Φ	<i>Minimization function of E_α</i>

Chapter 1

Introduction and literature review



1. Introduction and literature review

1.1. World energy outlook

The beginning of the industrial revolution in 1760 pushed the world toward the development of various sophisticated mechanical, chemical, and electrical processes and machines to be used for the fulfilment of manufacturing, transportation, domestic requirements of people around the world [1, 2]. This led to a rise in industrial infrastructure in different fields and created a huge demand for reliable and continuous supply of energy. The discovery of crude oil in 1875 drastically shifted the supply for fulfilling the rising energy demands throughout the world. From 1875 to the 21th Century, the usability and convenience of the fossil fuels shaped the modern world in every aspects of the modern world from industry to transportation, food to power industry, and military to domestic. However, heavy dependence on the fossil fuels viz. crude oil and natural gas, led to the crude oil crisis in 1973 [3]. Following the oil crisis, the world saw that extensive use of fossil fuel has led to an increase in the Earth's temperature due to continuous release of greenhouse gases, at a slow but alarming rate leading to the event of global warming. The rise in global energy demand, decrease in conventional fossil fuel reserves, and an alarming rise in global warming, encouraged the scientific community to search for and come up with alternative and sustainable hydrocarbon resources and clean fuel technologies. To preserve the conventional oil reserves, mitigate climate change and to fulfill the ever-rising energy demand, the focus was on conservation and management of the use of fossil fuels, adopt new and renewable energy sources such as biomass, waste, solar and wind, and explore the potential of the unconventional petroleum reserves scattered around the world. This led to the classification of different energy resources around the world into two broad classes, viz. Renewable and Non-renewable sources. The Non-renewable sources were further classified into two sub-classes as Conventional and Non-conventional sources (Fig 1.1).

Renewable energy fuels such as bio-diesel which can be obtained from various edible and non-edible biomass, contains high energy value and has zero emission, thus reducing carbon footprint. Solar and wind energy can be optimized to produce seamless electricity in the near future. But these renewable reserves are bound by limitations. The cost of generation of renewable energy and is high. The energy content of most renewable fuels is lower than fossil fuel. Geographical and climatic limitations restrain use of solar and wind energy to specific locations.

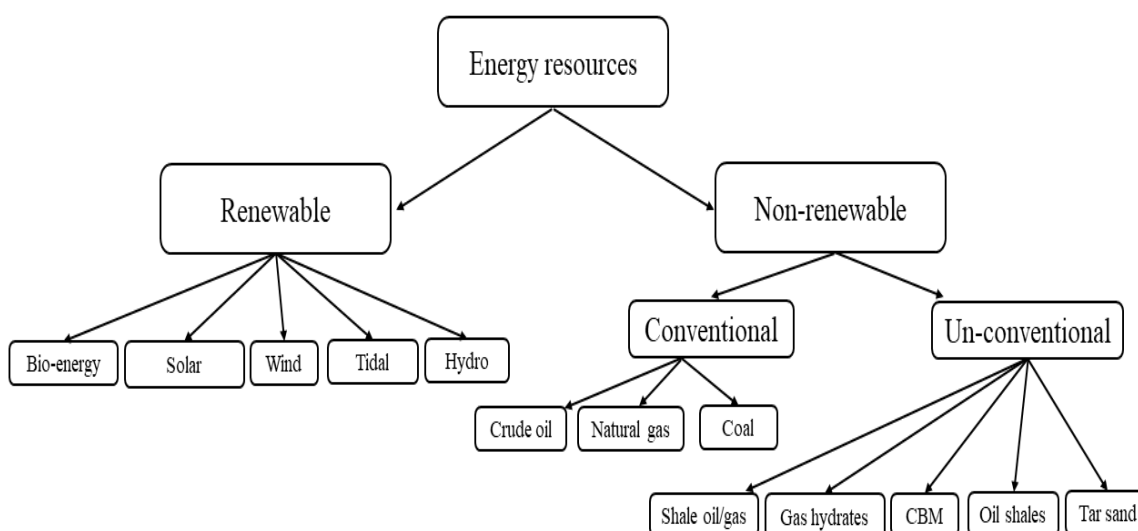


Fig 1.1. Classification of different types of energy resources.

1.2. Unconventional petroleum resources

Fossil fuels have established themselves as the most conventional source of energy to the modern world due to their high energy density. As an alternative to conventional petroleum resources, unconventional petroleum sources hold a large potential of untapped energy around the world. Unconventional petroleum sources may be defined as the sources of petroleum which cannot be obtained by conventional production methods. They promise high energy content and abundance, but are constrained by the utilization of high amount of energy into producing the petroleum oil and gas from the reserves and developing efficient and clean methods of production with minimum

harm to the environment. They are required to be heated or extracted by forced mechanical or chemical methods. Examples of unconventional petroleum sources are shale oil, shale gas, oil shales, tar sand, coal bed methane (CBM). In recent times the unconventional petroleum resources have gained their importance in the global energy framework and has emerged as a new theoretical frontier in the hydrocarbon industry [4]. The conventional petroleum reserves account to only 20% of the total hydrocarbon reserve, and the unconventional reserves contains the entire 80% of the total hydrocarbon reserve. The total global unconventional gas reserve has been calculated to be $3.9 \times 10^{15} \text{ m}^3$ consisting of shale gas, CBM, and gas hydrates[5]. The total global reserve of tight and heavy oil has been estimated to be 327×10^8 tonnes and 1027×10^8 tonnes, respectively[5]. The total reserve of oil sands have been calculated as 1067×10^8 tonnes [5]. Oil shales have the largest deposit in the world among the unconventional resources and are estimated to be 4540×10^8 tonnes spread over more than 600 reserves around the world[6]. But, these reserves also have their limitations. The technology for the recovery and processing of these resources is still in early stage, and not entirely economical.

1.3.Oil shale

Oil shale is an unconventional petroleum reserve which has come forward as a promising and viable and promising replacement to conventional petroleum [7]. Oil shale and oil sands can contribute significantly to energy requirements by producing unconventional oils through thermal treatment. The estimated recoverable oil from oil shales globally is 3.3 trillion barrels. Oil shale can be exploited as a viable source to produce oil and gas by pyrolysis and electricity by direct combustion. Oil shale is a complex heterogeneous material comprising of mineral matters with organic matters contained inside the pores. The organic matter is called kerogen. Kerogen is a complex organic compound which decomposes into bitumen which in turn decomposes into oil

and gases on application of heat. There has been active research in the production of shale oil from oil shales since the early 20th century. Currently, most of the commercial methods in operation or under development are direct heating retorts. In-situ production technologies have seen a significant revival with recent advancements in understanding the inherent technical logistics of the process. This involves a slow thermal pyrolysis of the organic matter in shale which leads to a light oil product that would not require additional thermal upgrading. The variability in composition and geologic setting of worldwide oil shale deposits affects the applicability of various technologies. Water content, minerals, and organic maturity (amount and H/C ratio) vary with source rocks causing different product distribution when subjected to retorting conditions [8]. There are around 600 oil shale deposits around the world with USA having the largest reserve and some of the most popular oil shales are Green River oil shale and Colorado oil shale. Other countries with significant oil shale reserves are Brazil (Irati oil shale), Australia (Queensland oil shale), Jordan (Sultani and Ellujun oil shales), Russia and China (Huadian oil shale). No comprehensive overview of the oil shale geographical allocation is available. More recent studies by the United States Geological Survey estimate that the three largest oil-shale deposits which are part of the Green River Formation. In India, oil shale occurs as outcrops in the coal mines of Upper Assam and Arunachal Pradesh region, with an estimated reserve of 137 billion tons with a recovery factor of 10% to 20% [9]. This untapped reserve acts as the source rocks for the oil field of Upper Assam India [10]. The estimation of different oil shale reserves around the world are summarized in Table 1.1.

Table 1.1. Distribution of oil shale reserves around the world (source: gsienergy, 2018).

Countries	Oil Shale	Oil shale reserve (billion barrels oil recoverable)
USA	Green River, Colorado	2118
China	Huadian	328
Russia	Bazhenov	271
Australia	Queensland	31
Brasil	Paraiba	52
Morocco	Tarfaya	37.8
Estonia	Kukersite	16.3
Canada	New Brunswick	15.2
India	Upper Assam	15

The extent of research in oil shale retorting is quite significant and covers different aspects of production of shale oil from analysis of raw material, kinetic study to studying effect of inorganics on the organic matters during pyrolysis. Current study in oil shale pyrolysis focuses on optimizing pyrolysis parameters, development of new retorting processes, investigation of catalytic effect of inherent mineral matters present in the oil shale during co-pyrolysis studies with other carbonaceous materials, and optimization of energy, exergy and cost balance of existing oil shale retorting processes.

1.4. Characterization of oil shale

Oil shale is a complex sedimentary rock which contains organic matter trapped inside its mineral matrix. The petrophysical study of oil shales helps in classifying different oil shales around the world. The presence of different mineral matters has a significant effect on the retorting of the oil shales, as some minerals may act as catalyst to the pyrolysis process others may act as inhibitors[11]. Based on its mineral matter composition, oil shales are classified as Carbonate-Rich, Siliceous or Cannel shale [10]. Bhargava et al. [12] studied the characterization of different

Australian oil shales and found the shale to be carbonate rich. Tiwari and Deo [13] studied the characterization, pore evaluation and thermal degradation of Green River oil shale. The oil shales of Green River and Colorado contains lesser sulfur, higher carbon and found the shales to be carbonate based. The oil shales of China viz. Huadian, Fushun and Nongan contain higher amount of clay and silica compounds and lesser amount of carbonates[14]. The Kukersite oil shale of Estonia, which is considered to be standard against which all other oil shales are graded contains higher amount of calcite and dolomite compared to silica compounds [15]. Israel has a large reserve of oil shales and their characterization shows the oil shales to be carbonate rich on comparison to Colorado oil shale which is also carbonate rich [16]. Similarly, the Jordanian oil shales are carbonate rich with considerable amount of quartz present in them [11]. The oil shales of upper Assam India are said to be siliceous in nature due to higher presence of clay and silica [10]. Solomon et al. [17] studied the oil shale properties using the FTIR spectroscopy. Bartley [18] analyzed the Rundle and Julia Creek oil shale of Australia using GC-MS analysis of the oils obtained from the oil shale samples. The generation potential of oil and gas from an oil shale is governed by the composition, maturation, and type of kerogen matter present in it. Wang et al. [19] studied the origin, maturity and depositional environment of the kerogen of the carboniferous shales of Quadam basin of China. Rock-eval analysis of the shale samples showed high total organic matter content and kerogen to be of type III with high maturity. Wang et al. [20] studied the structural characteristics of kerogen in different grade oil shales. The structural characteristics of the kerogens were studied from the aspects of aliphatic structure, aromatic structure and heteroatomic species. It was shown that with increase in density the ratio of aliphatic carbon and average methylene chain length of the kerogen increased, the substitutive degree of aromatic ring increases but the average size of aromatic ring and aromatic cluster decreased.

1.5. Pyrolysis of oil shale

The primary method for production of hydrocarbons from oil shales is by retorting or pyrolysis. In this method the oil shale samples are subjected to high temperature at a certain incremental rate from atmospheric temperature in an inert atmosphere commonly in the presence of nitrogen and held at the temperature for a certain period of time. Different researchers have studied the retorting processes and their outcome. During retorting of oil shales, with increase in temperature the organic compound or kerogen undergoes thermal degradation and gets converted into bitumen which gets converted into oil and gas under the influence of temperature. A schematic of the pyrolysis process of oil shale is presented in Fig 1.2.

1.5.1. *Pyrolysis mechanism of oil shale*

Kerogen is a complex organic material and is the precursor to petroleum [21, 22]. Fundamental study on the compositions and structure of the organic matter (kerogen) provides an insight into the maturation of oil shale and the potential compositions of the products produced by thermal degradation[23, 24]. The mineral matters present in oil shale plays significant role in retorting or pyrolysis of oil shale. Silica, carbonate, pyrite etc. can drastically govern the heat transfer in oil shale, and influence the composition of products formed during pyrolysis of oil shale [24-26]. The thermal decomposition of oil shale requires very high temperature. Decomposition of organic matter generally transpires from about 200°C to 600°C and the mineral matters start to decompose above 600°C [14, 27, 28]. Pyrolysis reaction conditions significantly influence product distribution and composition, hence the determination of suitable pyrolysis parameters is vital for obtaining the yield of desired composition[29, 30]. Oil shale degradation kinetics is significantly influenced by different variables, such as, heating rate, pyrolysis temperature, holding time, particle size, pyrolysis pressure, mineral matters existent in oil shale and type of reactor used for pyrolysis [16,

31-34]. The use of a well-controlled pressurized pyrolysis process has been proven effective for the production of high-value fuel from oil shale as well as other carbonaceous materials[35-37].

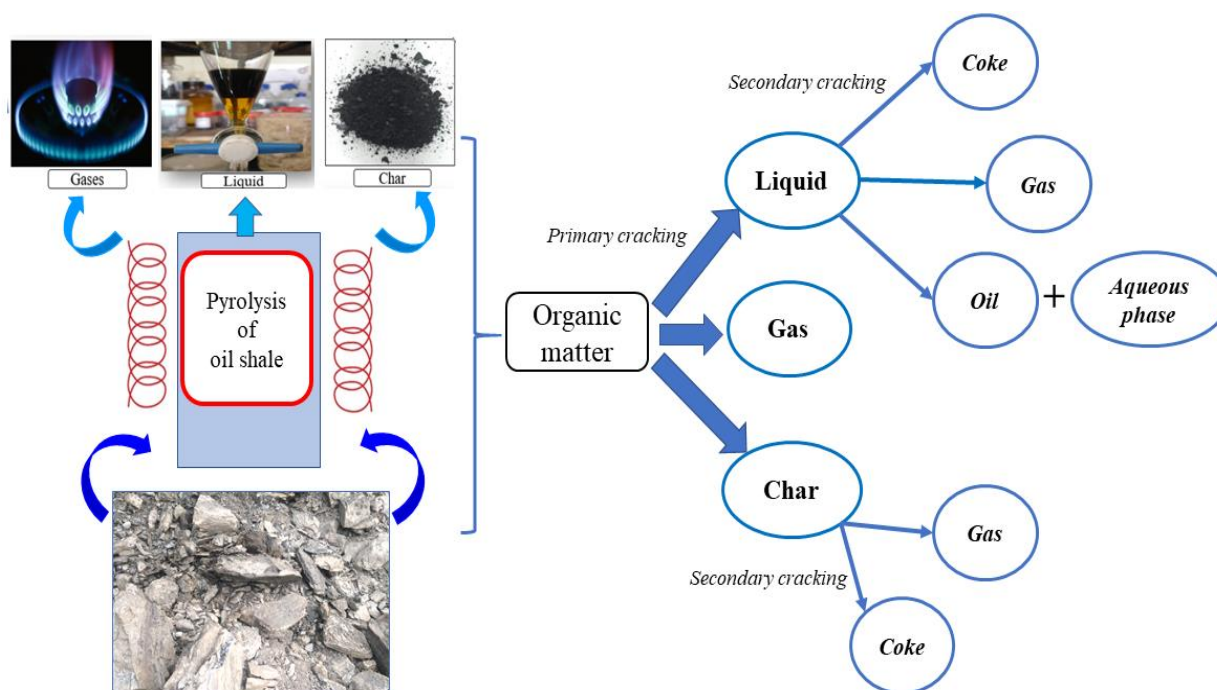


Fig 1.2. Schematic of pyrolysis mechanism of oil shale.

The thermal degradation of oil shale involves the occurrence of multiple parallel reaction models and variable activation energy values as the reaction progresses. The overall oil shale pyrolysis process is often studied by thermogravimetry (TG) for kinetic analysis. TG based thermal degradation kinetic is widely used for investigation of solid state degradation kinetics [38, 39]. Isoconversional methods recommended by the International Council of Thermal Analysis and Calorimetry (ICTAC) [38, 40] have been proven to give reliable kinetic data even when multiple reaction steps are involved. Isoconversional methods determine the distribution of activation energy values throughout the degradation process by considering the temperature dependence of isoconversional rate without assuming any predetermined reaction model. Previously, the degradation kinetics of different oil shale has been explained to occur following two consecutive

first order reactions [41-44]. The decomposition of Moroccan oil shale and its kerogen has been determined using model fitting and model free methods, and reported the oil shale to follow diffusion mechanism (D4) [45]. Study of the demineralization of Jordanian oil shale showed catalytic and inhibition behavior of the minerals present in oil shale [11]. Further, advanced isoconversional method has also been reported for the determination of oil shale pyrolysis kinetics [27, 46]. Campbell et al.[47] suggested the degradation mechanism of Colorado oil shale as a first-order reaction model. Peters et al.[48] studied the pyrolysis kinetics of kerogen from different origins, assuming multiple first-order reactions and nucleation models and using a distributed activation energy model. Burnham and Braun[49] reported generalized distributed models and isoconversional methods[38, 40, 50] to be suitable for the investigation of pyrolysis kinetics of kerogen because of its complex nature. The utilization of the isoconversional methods has been broadly reported for the identification of pyrolysis mechanisms for oil shale and kerogen[27, 51]. Detailed discussion the kinetics of oil shale pyrolysis process is presented in section 1.6.

1.5.2. *Degradation of kerogen in the absence of mineral matter*

The presence of the mineral matrix in oil shale has certain influence over the degradation kinetics of the oil shale and product formation and composition. To study the effect of mineral matter on the pyrolysis mechanism of oil shale, the oil shale samples are subjected to acid-solvent[52, 53] or alkali-acid[54-56] demineralization process. Both the demineralization methods have been proven to be highly effective acid-solvent for complete isolation of kerogen from the oil shale mineral matter matrix[53, 56]. The effects of mineral matter on kerogen pyrolysis have been critically discussed in the literature. Dembicki [57] studied the kinetics of demineralized kerogen from Kimmeridge black shale and reported that the presence of minerals such as quartz, calcite, and dolomite increase the activation energy, and kaolinite and montmorillonite decreases the activation

energy of the pyrolysis process. He also reported that the effect of mineral matter on kerogen decreases with an increase in the total organic carbon content above 2%. Reynolds and Burnham[58] studied the influence of mineral matter on kerogen pyrolysis kinetics for different oil shale samples worldwide and observed that the activation energy values of kerogen to be similar to that of the parent oil shale sample. Similarly, Pan et al.[59] reported the mineral matter to have no effect on the pyrolysis kinetics of demineralized Jimsar kerogen. The catalytic effect of different minerals on product yield and composition has been discussed previously[24, 26, 60]. Patterson et al.[24] reported a significant influence of subsequent mineral matter degradation over compositions and mechanisms of evolved products during thermal degradation. Yan et al.[61] and Liu et al.[62] studied the synergy of minerals and kerogen in product composition and yield. However, the occurrence of secondary cracking and delay in hydrocarbon volatilization temperature in the presence of minerals during kerogen and oil shale pyrolysis has seldom been discussed. A step-by-step representation of the different reactions occurring during the degradation of oil shale was discussed by Tiwari[8], and the same has been summarized in Table 1.2.

Table 1.2. Tabulation of different parallel reactions occurring during pyrolysis of oil shale[8].

Organic phase reaction	Reactant	Products
Moisture removal or loss of bound water	H ₂ O (s)	H ₂ O (v)
Primary reaction	Kerogen	Oil(l) + Gas(v) [H ₂ (v) +CH ₄ (v) + CO ₂ (v)] + H ₂ O (v) + Char(s)
Secondary cracking of char	Char	H ₂ (v) + CH ₄ (v) + ROC (s) +ROH(s)
Secondary cracking of oil	Oil (l)	H ₂ (v) + CH ₄ (v) ROC(s) +Coke (s)
Distillation and condensation of oil	Oil (l)	Oil(l) + Oil(v)+Gas(v)

Gasification of char	$\text{ROC(s)} + \text{CO}_2(\text{v})$	$\text{CO}(\text{v})$
Water-gas Shift	$\text{CO}(\text{v}) + \text{H}_2\text{O}(\text{v})$	$\text{CO}_2(\text{v}) + \text{H}_2(\text{v})$

*l = liquid; v = vapors; s = solid

1.5.3. Influence of pressure on pyrolysis mechanism of oil shale

The increase in pyrolysis pressure increases the hydrocarbon volatilization temperature and decreases the rate of vaporization of oil leading to delay in hydrocarbon expulsion and occurrence of cracking and secondary reactions. This phenomenon can be observed by the increase in apparent activation energy values[63, 64]. The increase of activation energy values with increase in pyrolysis pressure was also observed by Noble et al.[65]. However, Hillier and Fletcher[66] compared the pyrolysis kinetics of Green River oil shale at 1 bar and 40 bar, and reported no significant change in activation energy values. Similar results were also reported by Freund et al.[67] on the pyrolysis of Green River and Monterey origin kerogen samples. High-pressure influences product yield and composition due to the inhibition of hydrocarbon volatilization[35]. Corredor and Deo[68] reported a decrease in oil yield with increase in pyrolysis pressure. Burnham and co-workers[35, 64] conveyed similar findings for High-pressure pyrolysis of Green River oil shale. They reported that, with an increase in pyrolysis pressure, the oil yield decreased and the quality of oil increased, with less percentage of oxygenated compounds and aromatics. In-situ oil shale retorting processes are projected and developed to operate under different pressure-temperature conditions. Under such condition, it is desirable to understand the influence of pressure, pyrolysis temperature, and heating rate on pyrolysis kinetics, generation, and compositions of the products during pyrolysis of oil shale[64]. However, the use of these methods for investigation of pyrolysis kinetics under pressurized conditions has seldom been discussed.

1.5.4. *Pyrolysis mechanism of oil shale in the presence of water*

Oil shale can be considered as premature source rocks to conventional petroleum compounds. The process of hydrocarbon maturation from source rocks involves the conversion of organic matter to kerogen (diagenesis) by the influence of temperature and pressure, and subsequent conversion of kerogen into petroleum products viz. crude oil, and natural gas (catagenesis)[69, 70]. A comprehensive description of this process includes the degradation of the intermediate polar-rich bitumen phase formed by the decomposition of kerogen with cumulative thermal maturation that leads to the expulsion of hydrocarbon-rich products at higher degrees of thermal maturity[53, 71, 72]. The possibilities of investigating the chemistry of the oil generating processes and related reactions have expanded significantly to study and develop synthetic maturation processes to produce petroleum grade oil and gases from hydrocarbon source rocks[73]. The hydrous pyrolysis process developed by Lewan and team [71, 74, 75] helped produce pyrolytic products similar to petroleum crude. They stated that, during the formation of hydrocarbons, the presence of water promotes thermal cracking, inhibits carbon-carbon bond crosslinking reactions, and the presence of water in the source rock is vital in the generation and expulsion of an immiscible saturated-enriched oil phase. Therefore, the simulation of the catagenesis process of maturation of kerogen can be achieved by the hydrous pyrolysis process, where the long reaction time and slow reaction rates are substituted by short reaction time and high pyrolysis temperature[74-76]. Barth et al.[76] performed hydrous pyrolysis studies on Kimmeridge oil shale samples to simulate the catagenesis process of maturation of kerogen into oil and gases. Le Deon et al.[77] performed multiple hydrous pyrolysis experiments of green river oil shale samples to replicate the in-situ maturation of oil shales, and reported the produced oil samples to be highly aliphatic and with long chain alkanes and low polyaromatic compounds. Spigolon et al.[78] studied the maturation of lower cretaceous

Brazilian source rocks by hydrous pyrolysis to study the changes in properties of produced hydrocarbons through temperature range and residence time. Knauss et al.[79] used hydrous pyrolysis experiments to investigate the generation of carboxylic acids and light hydrocarbons from New Albany and Phosphoria oil shales samples and reported that the pyrolysis pressure had little effect on the yield of production of carboxylic acid compounds but had no influence over the generation of hydrocarbons. Conversely, Uguna et al.[80] and Wo et al. [81] reported that an increase in pressure during hydrous pyrolysis experiments of oil shales inhibited the generation of liquid products and further subdued the cracking reaction of produced oil. Lewan and Roy[71] investigated the effect of water in the maturation of kerogen into hydrocarbons by comparing the results of hydrous and anhydrous pyrolysis and reported that the presence of water did not show any effect on the conversion of kerogen to bitumen. However, it showed a significant impact on the conversion of bitumen into hydrocarbons. Rowland et al. [82] studied the generation of aromatics from hydrous pyrolysis of Kimmridge source rocks and reported high aromatics concentration. They also described the composition of the aromatic compounds to be similar to natural crude (i.e. alkylnaphtelenes and alkylated sulfur to aromatics). Leif and Somoneit [83] studied the hydrous pyrolysis of Messel shale (Germany) and observed that the kerogen breakdown to generates n-alkanes and terminal n-alkenes by free radical hydrocarbon cracking of the aliphatic compounds in the kerogen, which further undergo secondary cracking and isomerization to produce n-alkanes and heteroatoms. Pan et al. [84] studied the generation and yield of hydrocarbon and permanent gases from hydrous pyrolysis of Kukersite oil shale and kerogen sample and reported that the concentration of the produced, CO₂, and hydrocarbon gases increases with increase in water to oil shale blending ratio. The presence of organic sulfur affects the kinetics of petroleum generation due to the lower activation energies required to break C-S bonds and the

generation of sulfur radicals during that process, leading to earlier generation of bitumen and oil from sour source rocks for a particular temperature gradient relative to rocks containing less organic sulfur [85-87]. Birdwell et al.[88] studied the generation of different sulfur moieties at different pyrolysis temperatures. Lewan [89] and Abbott et al.[90] reported that the presence of elemental sulfur promotes the cracking of C-C free radicals, and oxidation of kerogen in the presence of water[91, 92] thereby influencing the formation of organic acids and carbon dioxide.

1.5.5. *Co-pyrolysis studies of oil shale with biomass for upgradation of pyrolytic products*

The decrease of fossil fuels and increase in global warming has encouraged the use of renewable and clean fuel technologies. Biofuels have been recognized as a favorable and sustainable renewable resource and can be extensively produced by pyrolysis of lignocellulosic biomass [93-95]. However, bio-oils produced from pyrolysis possess certain limitations, such as low calorific values and a high percentage of oxygenated compounds that lowers its heating value [96]. Previous studies have reported different methods for in situ upgradation of the oil samples produced from pyrolysis of lignocellulosic biomass by cracking of heavy fractions [72] as well as upgradation of the oil by hydrogenation to reduce their oxygen content using in-situ catalytic upgradation [97-99]. One such method for upgradation of bio-oils is by the process of co-pyrolysis with other carbonaceous materials [96, 100]. Oil shales samples from around the world have been used as a feed for co-pyrolysis process for their abundance of inherent mineral matter [87, 96, 101, 102]. Co-pyrolysis of oil shale and lignocellulosic biomass follows the multiple reaction models and is governed by the reactions involving transfer of free radicals from biomass to kerogen and the catalytic behavior of mineral matter present in oil shale on the produced bio-oil [96, 103]. During co-pyrolysis of biomass with oil shale, free radicals such as OH, and H are formed during biomass valorization, and are absorbed by the kerogen during degradation, leading to higher

concentration of aliphatic compounds. The mineral matter such as clay, illite, kaolinite, feldspar, and calcite present in oil shale are being reported to provide catalytic effect by inhibiting the production of oxygenated compounds [87]. The synergy during the co-pyrolysis of oil shale with biomass can be well understood by investigation of the pyrolysis process kinetics. During the valorization of lignocellulosic biomass, the process kinetics are governed by the simultaneous degradation of hemicellulose, cellulose, and lignin present in the sample. And, the kinetics of oil shale pyrolysis are influenced by the simultaneous degradation of kerogen and certain inherent clay minerals [72, 104]. The kinetic parameters of the co-pyrolysis studies of oil shale with lignocellulosic biomass samples can be well established using the isoconversional methods [38, 40, 72, 104, 105].

The utilization of oil shales as a feed for co-pyrolysis studies is not limited with lignocellulosic biomass samples. Different studies have been reported in literature regarding the co-pyrolysis of oil shale with other carbonaceous materials[106-110].

1.6. Factors influencing oil shale pyrolysis process

The pyrolysis process of oil shale is governed by different pyrolysis parameters such as pyrolysis temperature, heating rate, pyrolysis pressure, particle size, retention time, reactor design etc. The influence of the process parameters on the yield and composition of the produced products are summarized below.

1.6.1. Effect of temperature and retention time

Fengtai et al [111] studied the evolution of pore structure of the Huadian oil shale from 100°C to 800°C. They observed change in porosity and permeability with increase in pyrolysis temperature. They observed the fractures to change drastically from 350°C to 500°C. Saif et al. [112] studied

the microstructural evolution of the oil shales during and after pyrolysis. They observed significant increase in anisotropic porosity from 400°C to 500°C with the formation of micro-scale connected channels developed along the kerogen rich lamellar structure. Ribas et al. [113] studied the Irati oil shale before and after pyrolysis. They pyrolysed the oil shale by introducing the sample to a gas stream at 500°C to induce pyrolysis effect. Before and after analysis of the oil shale sample showed that the pyrolysis process had more effect on the petrofabric properties increasing the cracks and porosity and permeability. Gerasimov et al. [114] studied the pyrolysis of the Kukersite oil shale in an experimental setup using silica sand as solid heat carriers. The study was carried to study the primary heat transfer between the oil shale and the solid heat carrier in presence of expulsion of volatile matter. The maximum shale oil yield obtained was 73% at 560 °C. This showed the pivotal role of heat diffusion during pyrolysis and its impact on maximum product yield. Jiang et al. [115] studied the effect of hydrothermal pretreatment and their effect on the produced pyrolysis products. They considered the Huadian oil shale and pretreated it at 200 °C for 1 hour to 2.5 hours. They observed the maximum oil yield when the oil shale was pretreated for 2 hours. Analysis of the products showed the increase in percentage of aliphatic compounds with increase in hydrogen number and higher H/C value indicating higher energy content. Another useful analysis technique is the TGA-FTIR, which gives an evaluation of the evolved products during pyrolysis. Yan et al. [61] studied the catalytic effect of the mineral matters during pyrolysis and combustion of the Huadian oil shale and the kerogen using TGA-FTIR analysis. They observed the reduction in sulfur compounds in the presence of calcite minerals. Li et al. [108] studied the co-pyrolysis of oil shale with two types of coal viz. bituminous and lignite from 100 °C to 950 °C at 30 °C/min heating rate. They observed the increase in yield of product to 1.4% with optimum oil shale percentage in the mixture to be 50%. Alhesan et al. [116] presented a

comprehensive study on the effect of temperature and time on the pyrolysis of Jordan oil shale, by carrying out delayed low temperature pyrolysis. Grounded oil shale samples were heated isothermally at temperature range of 240 – 320 °C, with holding time of 7, 14 and 28 days. Lowest yield was obtained at 240 °C and holding time of 7 days. Pyrolysis temperature of 260 °C gave similar product yield to 240 °C for holding time of 14 and 28 days. It was reported that at pyrolysis temperature of 260 °C the asphaltene yield decreased with increase in reaction time to 28 days. The products obtained at temperature of 300 and 320 °C for 14 days showed presence of smaller molecules than the products obtained at lower temperature. Thus, showing that the fewer stable isomers were converted to more stable smaller isomers with subsequent increase in temperature.

1.6.2. *Effect of heating rate*

Heating rates greatly influence the pyrolysis of oil shales and the significance can be visualized by thermogravimetric analysis. Nazzal [33] studied the effect of different heating rates on Jordanian oil shales. He studied the pyrolysis in a fixed bed reactor and considering heating rates from 2°C/min to 30°C/min up to 520°C and observed that the oil yield increased up to 10°C/min but decreased as it reached 30°C/min. Noble & et al. [117] studied the effect of variable pressure under isothermal heating condition. They observed that the percentage of oil yield decreased with increase in pressure.

1.6.3. *Effect of particle size*

The influence of particle size during oil shale pyrolysis process has been studied extensively as solid and gas carriers[118, 119]. The pyrolysis processes where the particle size is considered as solid heat carriers, the size of the oil shale particles generally range up to <12 mm, however the gas carrier pyrolysis processes considered oil shale samples in the size range of 6 mm to 70mm. Therefore, the particle size of oil shale plays an important role in determining the desired yield and

composition of products[119]. Ahmad et al.[120] considered oil shale particle in the range of 0.5 mm to 10mm, and reported that increase in particle size resulted in increase of oil yield and decrease in gas yield. Nazzal [121] reported similar finding for the pyrolysis of Sultani oil shale, where he reported the increase in oil yield with increase in oil shale particle size from 0.22 mm to 5.60 mm. Han et al. [122] reported that for pyrolysis of three different Huadian oil shale samples considering oil shale particles of size 0.28 mm to 5 mm, the maximum oil yield was obtained for particle size <3mm, and either increasing or decreasing the particle size decreased the oil yield. Pan et al. [119] however reported that the particle size of the oil shale did not have any effect on the yield and composition of the pyrolysis products. Degirmanci and Durusoy[123] reported that, oil shale samples of smaller particle size showed lower activation energy implying the smaller particle size oil shale samples to be more reactive as compared to larger particles.

1.6.4. *Effect of inherent mineral matter*

The presence of different mineral matters was studied as to determine how their presence and effect of their individual thermal conductivities changes the overall thermal conductivity of the oil shale. As the pyrolysis of oil shale is affected by various conditions different methods have been developed in the field of oil shale retorting to account for those effects. Strizhakova and Usova [124] presented a review on the current trends in oil shale pyrolysis and their advantages and limitations on production of shale oil. Sun et al. [125] studied the oil yield percentage and the bulk geochemical parameters of the from the Songlio and Huadian Basin. The analysis was done using the TOC content, oil yield, semi coke content, gas loss, bulk density, pyrolysis value and Hydrogen Index (HI) to establish a grade for the oil shale samples. Guo et al. [23] studied the effect of the mineral matter in the self-heating retorting of oil shale and its effect in the production of shale oil. Pan et al. [59] studied the effect of mineral matter in the thermal decomposition of Jimsar oil shale

by using TG-MS technique. They analyzed the products formed during pyrolysis and inhibition and generation of different gases due to presence of certain minerals. In the present time researchers are focusing in the development of better retorting systems, modified pyrolysis methods and study the oil shale structure before and after pyrolysis. The pore structure of the oil shales changes drastically after pyrolysis and it plays a major role in heat and mass transfer during the pyrolysis process. Chang et al. [126] studied the effect of inherent mineral matrix on product yield and composition during pyrolysis of Huadian oil shale. The oil shale samples were subjected to stepwise demineralization process for removal of carbonate and silica minerals. Both the raw oil shale and demineralized oil shale samples were subjected to pyrolysis and the product yield and composition were compared. It was stated that carbonate minerals promote high yield of shale oil, and silicates prohibit the expulsion of shale oil. Silica minerals promotes cracking and aromatization of aliphatic hydrocarbons. This leads to increase in short chain hydrocarbons and aromatic hydrocarbons in the produced oil sample.

1.6.5. *Effect of reactor design*

Sohn and Shih [127] worked on providing a mathematical solution to the retorting of block oil shales considering internal temperature gradient. Solomon et al. [16] studied the effect of pyrolysis parameters on the quality and quantity of the products extracted from Israeli oil shale. They considered different factors such as heating rate, reactor geometry, retention time, temperature and pressure and varied these conditions to obtain the optimum process conditions and reported that the cracking and coking of the pyrolysis products were minimum when the temperature and retention time were kept at their minimum. Mehmani, Burnham, and Tchelepi [128] studied the thermal conductivity of the Green River oil shale. They prepared optical photographs to determine

the total kerogen content and developed a mathematical relation between thermal conductivity to the geological bedding grade and temperature of oil shale.

1.7. Kinetic study and modelling of oil shale pyrolysis process

The decomposition of organic matter in the oil shales is a complex process. Initially, with application of heat the kerogen decomposes into bitumen and subsequently the bitumen decomposes into oil and gases. This thermal decomposition of oil shales require very high temperature as the decomposition of organic matter generally occurs from about 200 °C to 600 °C and the mineral matters start to decompose from about 600 °C to about 1000 °C [14], [28], [27]. This decomposition can clearly be visualized by analyzing TGA curves. Thus, studying the kinetic parameters of oil shale pyrolysis is of pivotal importance. Different researchers have attempted to determine the steps of decomposition of organic matter and study the kinetics of the process. Skala et al. studied the modeling of oil shale pyrolysis by considering single-step, two-step and multi-step decomposition by considering conversion of kerogen and bitumen originally present in the oil shale to be converted into oil and gas to be the single step model and the conversion of kerogen to bitumen and from bitumen to oil and gas of formation of subsequent products from kerogen and bitumen individually to be two-step and multi-step conversion models respectively [42]. Aboulkas and Harfi [45] studied the decomposition of oil shale and kerogen of Morocco. They studied the decomposition of the oil shales and kerogens at different heating rates and used Coats and Redfern Method, Kissinger-Akahira-Sunose, Freidman, and Flynn-Wann-Ozawa to determine the activation energies for both oil shale and kerogen. Al-Ayed et al. [129] studied the pyrolysis kinetics of Ellajun oil shales of Jordan by using variable activation energy method by considering a modified first order reaction of organic decomposition of the oil shale. They also prepared a mathematic model called PYROL for simulating the mechanism of oil generation and expulsion

from oil shales which presented a clear insight of the different parallel reactions which occurs during pyrolysis of oil shales and the formation of different products [130]. Tiwari and Deo [46] studied the kinetics of pyrolysis of Green River oil shale by analyzing TGA data using Advanced Isoconversional method and concluded the method to be much efficient than other methods [27]. Braun and Burnham [44] studied the kinetics of oil shale pyrolysis of Colorado oil shale by using a fluidized bed reactor considering two parallel first order reactions. Braun and Rothman [131] studied the kinetics and mechanism of oil shale pyrolysis. They considered the model of decomposition to be two first order reactions and derived the activation energy for each reaction. Ekstorm and [41] Callaghan studied the pyrolysis kinetics of two Australian oil shales considering the decomposition to be two first order reactions with dependence to temperature and particle size. Harahsheh et al. [11] studied the effect of demineralization and variable heating rates on the kinetics of pyrolysis of Jordanian oil shales. They studied how the minerals present may act as catalyst or inhibitors for decomposition of organic matters and their effect on the activation energy of decomposition. Kharfi [132] studied the kinetics of Sultani and Ellujan oil shales of Jordan under isothermal conditions considering two first order reactions to be occurring during the decomposition. Torrente and Galan [133] studied the kinetics of Spanish oil shale using both isothermal and non-isothermal heating conditions in performing the TGA of the oil shale at three different particle size. For analyzing the kinetic parameters, they considered the Direct Arrhenius Plot Method, Integral Method and Differential Method. Aboulkas et al. [134] performed co-pyrolysis of Jordanian oil shale and plastic and compared their thermo-gravimetric data with that of the oil shale and plastic individually at variable heating rates. They tabulated the maximum degradation temperature for the co-pyrolysis of oil shales with different types of plastic and derived the kinetic parameters using Arrhenius method. Jankovic[135] studied the kinetics of non-

isothermal kinetics using the Weibull probability mixture model. Moine et al.[136] studied the multistep process kinetics of non-isothermal pyrolysis of Moroccan oil shale using TGA-DTG data. The analysis was carried out from 350°C to 600°C. The kinetic study was conducted using model free isoconversional methods, Coats Redfern method and master plots were used to determine the kinetic mechanisms. The n^{th} order model satisfied the pyrolysis process with $n=1.67$. Also the thermal oxidation of the Moroccan oil shale was studied by Moine et al.[137]. The co-pyrolysis kinetics of sewage sludge and oil shale was performed by Lin et al.[107]. The sewage sludge and oil shale mixture was set in the range of 10% to 90% and was heated from 100°C to 1000 °C at three different heating rates. The kinetic study was performed by KAS method and Starnik method. The optimum proportion of sewage sludge was set at 10% as it showed the lowest activation energy of 253.6 kJ/mol and 253.3 kJ/mol by Starnik and KAS method respectively. Foltin et al. [138] studied the dependence of kinetic parameters on conversion progress. The activation energy of the pyrolysis reaction varies with conversion. They reported a progressive increase in activation energy with increase in conversion. The production of oil and gas during pyrolysis of oil shale is a multi-pathway process. The change in the ratio of the pathways would result in change in activation energy. The more energy demanding pathway will increase the temperature. Thus, higher activation energy is observed with conversion towards higher temperature. Again, kerogen is a mixture of multiple compounds. The calculation of the kinetic parameters for the overall decomposition of the organic matter content is a contribution of numerous compounds with a synergistic effect on one another. Therefore, activation energy can be used as a distribution pattern conversion of different fragments of kerogen.

1.7.1. Modelling of oil shale pyrolysis process

Different researchers have put forward different models regarding the decomposition of organic matter during pyrolysis. Skala et al. [42] studied the modeling of oil shale pyrolysis by considering single-step, two-step and multi-step decomposition by considering conversion of kerogen and bitumen originally present in the oil shale to be converted into oil and gas to be the single step model and the conversion of kerogen to bitumen and from bitumen to oil and gas of formation of subsequent products from kerogen and bitumen individually to be two-step and multi-step conversion models respectively. Again, another important factor influencing oil shale pyrolysis is the heat and mass transfer through the oil shale particles during retorting. Han et al. [34] studied on heat and mass transfer in the oil shales based on different particle sizes of oil shales and prepared a mathematical model to evaluate the variation of heat and mass transfer. Pyrolysis of oil shale is done in both surface and in-situ. Different researchers have worked on the two pyrolysis methods and some have stated the in-situ conversion to be more economical compared to surface retorting. Gregg et al. [139] prepared a lab scale in situ pyrolysis model by considering oil shale block of Colorado oil shale and heating it up to 900 °C isothermally and observe the degradation. Hui et al. [140] performed a numerical simulation of in-situ oil conversions of North-East China oil shales. They calculated the transformations at different heating rates and concluded that in-situ retorting for 6 to 8 years will lead to 90% conversion of the oil shales. Li and Qian [32] performed pyrolysis of Maoming oil shales of China under isothermal heating and prepared a pyrolysis kinetic model considering both pyrolysis reaction and intraparticulate heat transfer and further studied the effect of variable heating rate and particle size on pyrolysis. The formation of pores in the oil shale during pyrolysis defines the flow of the pyrolysis products. Tiwari and Deo [141] studied the pore structure characteristics of the green river oil shale before and after pyrolysis and found out that

the heating temperature has a direct effect on the permeability of the pores during and after pyrolysis. Feteris and Sitnai [142] performed computational studies and simulations on the pyrolysis of oil shale particles ranging from single particle to cluster of particles considering the Julia Creek oil shale.

1.8. Optimization of oil shale pyrolysis process

As stated earlier, pyrolysis is the most effective and economical process for producing valuable products from oil shale. Although, the pyrolysis or retorting of oil shale is an energy intensive process. Large amount of energy is required to heat the oil shale up to a particular temperature to produce oil and gas. To fulfill the current energy demand, it is eminently imperative to reduce the energy consumption by subsequently increasing the yield of valuable products. Therefore, optimization of pyrolysis parameters and validating the energy and cost analysis of the optimized process is crucial for industrial utilization of oil shale pyrolysis. Not much work has been done on optimization of oil shale pyrolysis process, as well as on the energy and cost balance estimation of the same. Wang et al. [143] performed the exergetic life cycle assessment of Fushun type retorting system for optimization of its various limitations such as, low resource utilization efficiency, environmental sustainability, and shale oil production. The simulation studies were carried out using ASPEN Plus software. To increase the efficiency of the cycle the retorting temperature is to be controlled to 500 °C and the feed air saturation should be set at 80 °C. Mu et al. [144] studied both exergy as well as energy analysis of a combined fluidized bed retorting system and circulating fluidized bed combustion system, based on Chinese comprehensive utilization system, in ASPEN Plus on Huadian oil shale. The highest exergy efficiency was observed to be in the range of 460 – 490 °C. The Chinese comprehensive utilization system proved to be more efficient than the Fushun type retorting system. The temperature of recycled oil shale ash significantly affected the oil yield.

It was observed that the yield of oil decreased if the temperature of recirculating ash decreased under 820 °C. The simulation showed that retorting temperature is the governing parameter in increasing yield of products. Luo et al. [145] performed exergy analysis on hydrogenation of shale oil obtained from pyrolysis of oil shale, using ASPEN plus. The authors have presented a comprehensive overview by simulation and modelling of shale oil upgradation and examining the kinetics of hydrogenation process. The developed model showed exergy efficiency of 69.20%, with yield of 16.13% naphtha and 80.19% diesel. Optimization of the developed mode increased the exergy efficiency to 69.77% and increasing the total yield to 96.85% from 96.22%. The majority of the supplied energy was consumed by the furnace (59%) and the compressors (24%). The yield of naphtha products was increased by increasing the temperature and pressure; but it led to consumption of higher energy, thus increasing exergy destruction of the hydrogenation system. The optimum temperatures obtained for hydrocracking and hydro refining reactor were 350 – 375 °C and 375 – 400 °C respectively. The optimum pressure for both the units was set in the range of 16 – 17 MPa. Corredor and Deo [68] examined the effect of vapor liquid equilibrium in product distribution during oil shale pyrolysis. They presented a five-reaction network equilibrium for the primary and secondary reactions occurring during oil shale pyrolysis using MATLAB to investigate the effect of heating rate and pressure on the volatilization of the organic matter. The developed model functionality was based on Peng-Robison equation of state, Gibbs tangent plane criterion used for phase stability and Rachford-Rice flash calculation. The heating rate and pressure were set in the range of 0.001 °C/min – 10 °C/min and 14.7 – 500 psi. The oil yield to be obtained was expected to be less in case of powdered sample than bulk core, as powdered samples are unable to generate pore network for expulsion of vapor phase generated during pyrolysis. It was stated that with increase in pressure the oil yield decreased, irrespective of heating rate.

Further, secondary cracking reactions can be prevented by removal of evolved vapors. It was concluded that 50% removal of vapor resulted in 97% oil yield of the maximum yield for 0.95 of mass fraction of vapor phase removed.

1.9. Summary and research gap

Significant amount of research has been conducted in characterization of oil shale around the world, However the structure and composition of kerogen present in the oil shales has not been established. The quantification of compounds present in kerogen can be estimated by solid phase NMR spectroscopy, yet the compositional identification has still not been achieved. It has been reported extensively about the occurrence of multiple parallel reactions during oil shale pyrolysis, nevertheless no study has been shown on the cause of these parallel reactions, their effect in product yield and composition and how these secondary reactions can be limited. The composition of the oil shale determined by elemental analysis, does not directly reflect the composition of the yield obtained. Oil shale pyrolysis is predominated by conductive and convective heat transfer, which is preceded by mass transfer. No adequate work is present in the representation of real time heat transfer effect on the mass transfer and phase change inside the mineral matrix, which leads to expulsion of oil and gas. The kerogen present in oil shale and source rocks is bound with the mineral matter and decomposes simultaneously. There is significant interest and debate about prospective variance in kinetic parameters obtained from pyrolysis of parent oil shale and isolated kerogen. Another issue is whether the minerals catalyze kerogen decomposition to delay the vaporization temperature of hydrocarbons, leading to the occurrence of coking and cracking reactions. Also, the acid treatment used for the extraction of kerogen might lead to the breakdown of some bonds in the kerogen, thereby changing the pyrolysis kinetics. Therefore, a detailed study

on the maturation pathway of kerogen and a thorough understanding of its synergy with inherent minerals is of significant importance.

Oil shale pyrolysis process is significantly influenced by pyrolysis temperature, heating rate, and pyrolysis pressure. The increase in pyrolysis pressure increases the hydrocarbon volatilization temperature and decreases the rate of vaporization of oil leading to delay in hydrocarbon expulsion and occurrence of cracking and secondary reactions. This phenomenon is well observed by the distribution of the kinetic parameters. However, the effect of pressure on pyrolysis kinetics of oil shale has seldom been discussed.

A variety of techniques have been reported to measure oil and gas generation kinetics for kerogen pyrolysis, although the detailed information for individual pyrolysis products is not provided adequately. The latter is of significant importance to provide an insight into the possible structure of kerogen and understand the expulsion ratio of oil to gas during the maturation of kerogen. This information will further help to establish the cause of the variation in distribution of activation energy, and modelling of secondary reactions in the presence of inherent minerals. Also, the presence of water during pyrolysis increases the pressure due to steam formation and may also act as a source of hydrogen and thereby influence the composition and yield of the produced oil and gases.

Co-pyrolysis of oil shale with other carbonaceous matters has shown oil shale to exhibit catalytic properties due to the presence of inherent minerals. The catalytic effect is more prominent and influential in co-pyrolysis of oil shale with lignocellulosic biomass. During co-pyrolysis process, the cynical process parameters which affect the yield and composition of the pyrolysis products are pyrolysis temperature, heating rate, and feed blending ratio. To study the influence of these process parameters on the yield of pyrolytic oil and gases, different optimization techniques have

been reported in literature. To understand the synergy mechanism of the co-pyrolysis process, it is critical to investigate the interaction of different pyrolysis process parameters on the yield and composition of different pyrolysis products.

Fulfilling the above limitations will lead to a complete and sustainable use of oil shale as a fuel of the future; which has the potential to fulfill the energy demand and preservation of the environment, defining it as a clean fuel.

1.10. Objectives

Based on the identified research gaps, the following objectives have been formulated to present a comprehensive study on the pyrolysis mechanism of oil shale and, project the considered Indian oil shale sample as a source of sustainable and clean energy.

1. Detailed characterization and lab-scale pyrolysis of Indian oil shale: Hydrocarbon generation potential, and optimization of process parameters
 - 1.1. *Physicochemical and thermochemical characterization of oil shale sample.*
 - 1.2. *TG based kinetic analysis.*
 - 1.3. *Benchmarking pyrolysis process parameters and characterization of products.*
2. Isolation of kerogen to investigate the maturation mechanism of oil shales in the subsurface.
 - 2.1. *Isolation of the organic matter or kerogen from the oil shale.*
 - 2.2. *TG based kinetic study, and pyrolysis of isolated kerogen and product characterization.*
 - 2.3. *Comparison of the composition of pyrolytic products from isolated kerogen and oil shale*
3. Investigation of the influence of high-pressure on the kinetics of oil shale pyrolysis and product yield and composition.

3.1. Thermochemical degradation of the oil shale sample for investigation of pressure on pyrolysis kinetics.

3.2. Lab-scale High-pressure pyrolysis and investigation of products yield and composition.

4. Soaking and hydrous pyrolysis studies of oil shale samples to visualize the effect of water on product yield and composition.

4.1. Soaking and hydrous pyrolysis experiments: the effect of water on product and composition of yield at sub-critical condition.

4.2. Investigate the effect of water salinity on the yield and composition of yield

5. Co-pyrolysis studies of Indian oil shale samples with waste lignocellulosic biomass to study the catalytic properties of oil shale and its inherent minerals.

5.1. TG based kinetic analysis of co-pyrolysis process at oil shale to biomass blending ratios

5.2. Use of Design of Experiments for the design of lab-scale experiment matrix.

5.3. Use of response surface methodology for the optimization of pyrolysis parameters to maximize oil yield with low organic acids.

1.11. Thesis Outline

Chapter I provides an *Introduction and Literature* review oil shale, and different pyrolysis techniques, with a brief discussion on the effects of different pyrolysis process parameters, and kinetic study.

Chapter II presents elaborate description of the origin and physiology of the oil shale sample, with a comprehensive description of the methodology of different physicochemical and thermochemical characterization techniques, different lab-scale pyrolysis processes, and theory for the kinetic study of the pyrolysis processes.

Chapter III summaries the detailed physicochemical and thermochemical characterization of the oil shale sample and, the isolation of organic matter or kerogen form the oil shale sample for characterization and kinetic study. The lab-scale pyrolysis of the oil shale sample has been performed for estimation of hydrocarbon generation potential, and investigation of the kinetics of the pyrolysis reaction mechanism. The pyrolysis mechanism of oil shale and isolated kerogen is compared to investigate the maturation mechanism of oil shales in the subsurface, and visualize the generation of hydrocarbons from source rocks in the subsurface.

Chapter IV reports the pyrolysis mechanism of the oil shale sample in the presence high-pressure for investigating of the influence of pressure on the kinetics of oil shale pyrolysis, product yield and composition of the produced products.

Chapter V discusses the effect of water and its salinity on the product yield and composition during maturation of oil shale in the Earth's subsurface. The oil shale samples were subjected to Soaking and hydrous pyrolysis studies under pressurized conditions to visualize the effect of water

on product yield and composition, by simulating the catagenesis conditions which occur during the maturation of source rocks in the subsurface.

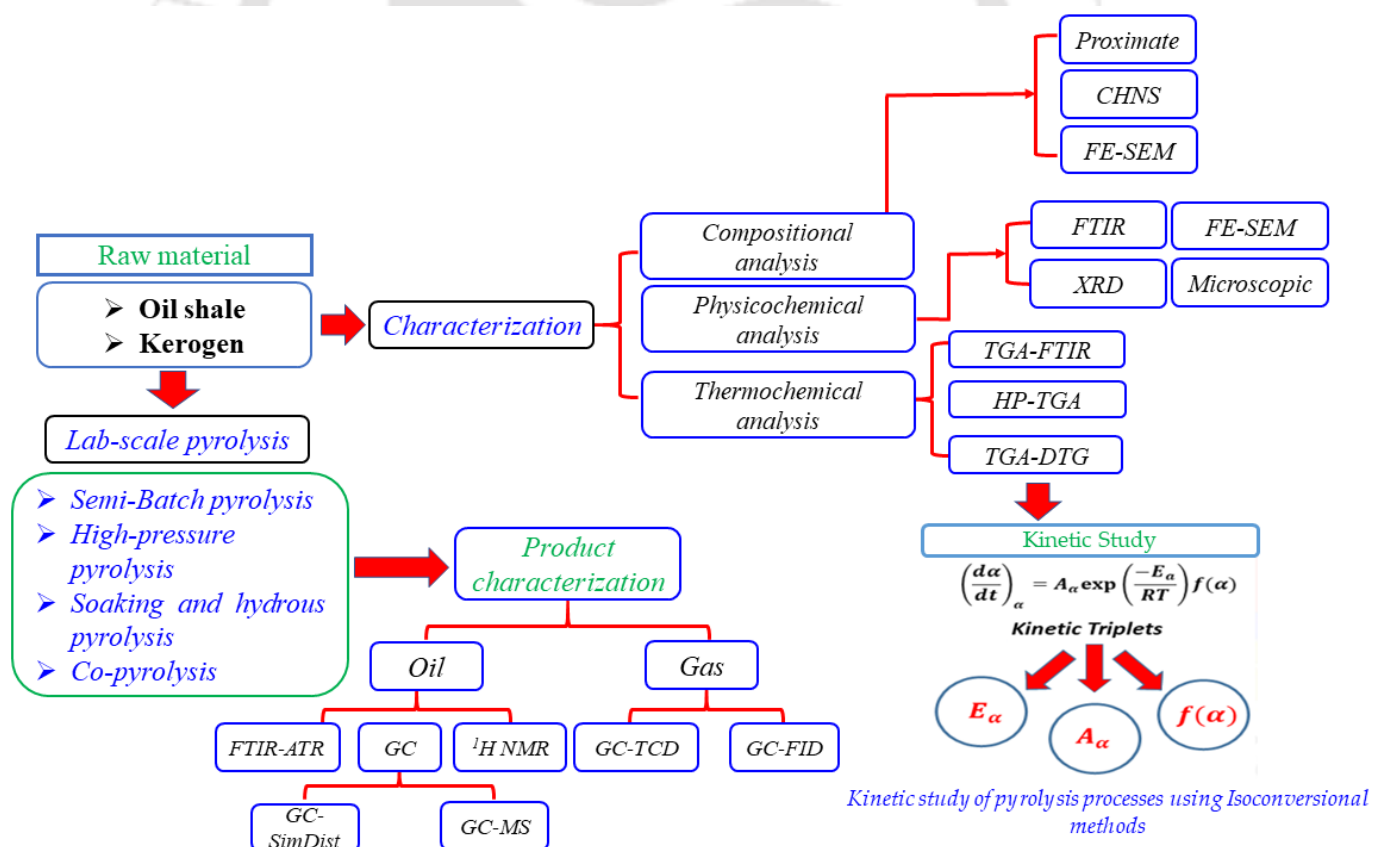
Chapter VI investigates the catalytic properties of the inherent minerals in the oil shale during co-pyrolysis of oil shale with lignocellulosic biomass. To study the same, co-pyrolysis studies of the Indian oil shale sample were performed with rubber seed shell which are treated as waste biomass.

Chapter VII. summarizes the conclusion drawn from the present work and provides a possible direction and recommendations for future work with a small description of the probabilities of catalytic pyrolysis for targeted upgradation of pyrolytic oil and gases obtained from the oil shale sample and thereby justify the oil shale sample as a potential feed stock for production of high energy density fuel.

Chapter 2

Materials and methodology

- Materials
- Experimental procedure
- Kinetic modelling and theory
- Lab-scale pyrolysis
- Product characterization
- Analytical techniques



2. Materials and methodology

This chapter presents an introduction to the feedstock (Indian oil shale sample) and the organic matter or kerogen, its origin, and a comprehensive description of different physicochemical, thermochemical, and petrographic characterization techniques used for characterization of the feedstock, and pyrolysis products. Different thermogravimetric techniques were used for the thermochemical characterization of the sample under different pyrolysis conditions and their methodologies have been discussed elaborately. The thermogravimetric data were used for determination of the pyrolysis kinetic parameters under different pyrolysis conditions. Different lab-scale pyrolysis experiments were designed to target selective studies and an elaborate and step-by-step explanation of the procedure of different pyrolysis techniques and processes which have discussed in details. The pyrolysis products were characterized by using various standard analytical techniques and the same have been conferred in details.

2.1. Materials

2.1.1. Oil shale and kerogen

Oil shale samples were collected from the East mine of Tikak Colliery, North Eastern Coal Fields, Margherita, Assam, India (Coal India Limited) (Fig 2.1 (a)). The oil shales are found interblended among the coal seams (Fig 2.1(b)). They appear as outcrops during mining of coal, and are considered as overburden to the coal. These oil shales are termed as carbonaceous shales, and are considered to be the principle source rocks for the existing hydrocarbon fields of North Eastern India [10, 146]. The oil shales samples possess a brown to dark brown texture with black streamlines appearing on the surface. The procured samples were grounded using a mechanical jaw crusher followed by a hammer mill crusher and screened to 150 microns (100 mesh) size prior to characterization, and pyrolysis experiments. The organic matter or kerogen trapped inside the

mineral matter matrix of the oil shale was extracted from the grinded oil shale sample by following acid-solvent demineralization process (Detailed is in Section 2.2).

2.1.2. Solvents and acids

The solvents and acids used for demineralization of oil shale, and for recovery and washing of liquid products during the different pyrolysis processes were methanol (CH_3OH) and dichloromethane (DCM), hydrochloric acid (HCl), nitric acid (HNO_3), and hydrofluoric acid (HF) of ACS grade and procured from Merck Life Sciences Pvt. Ltd.

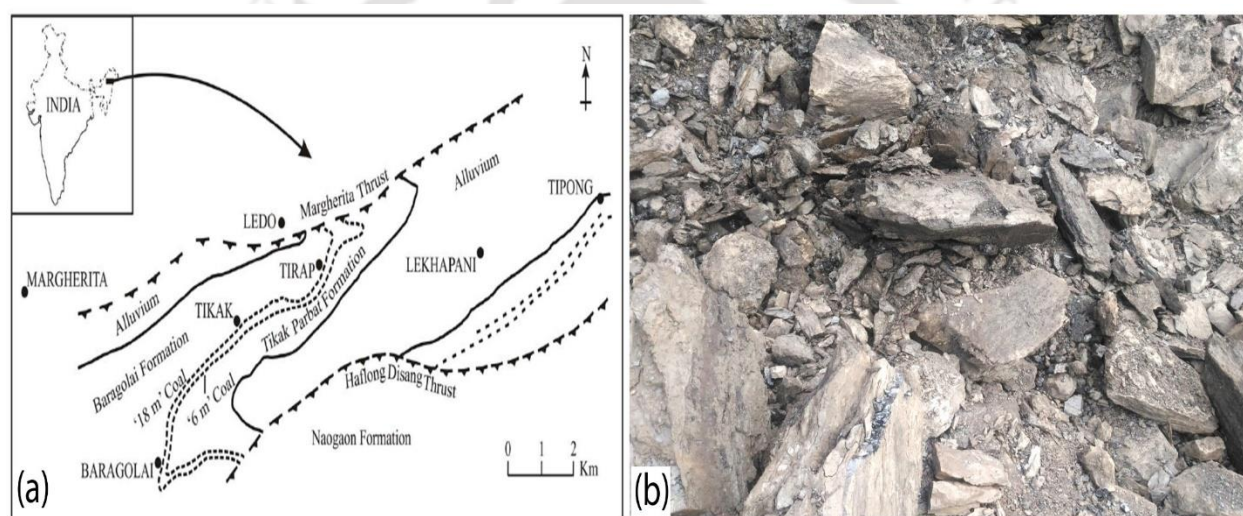


Fig 2.1. (a) Geographical map of Makum Coal Field, Margherita, Assam, India [146] (b) Oil shales in Tikak Colliery, Makum Coal Fields, Margherita, Assam, India.

2.2. Demineralization of oil shale sample: Extraction of kerogen

The grounded oil shale samples were treated to acid solvent demineralization process for removal of the mineral matter. Demineralization of oil shale is a multi-step process of solvent extraction and acid leaching. The flowchart of the step by step demineralization process is presented in Fig 2.2. The solvents used in this process were methanol (CH_3OH) and dichloromethane (DCM).

Three acids viz., hydrochloric acid (HCl), nitric acid (HNO₃), and hydrofluoric acid (HF) were used to dissolve the carbonate minerals, pyrite, and silica minerals, respectively[11, 59, 61]. 50 g of raw oil shale sample of 100 mesh size was considered. In this first step, bitumen extraction was achieved using Soxhlet extraction with 1:4 (wt/wt) methanol (CH₃OH): dichloromethane (DCM) for 24 hours. The bitumen-free oil shale was leached for 48 hours at room temperature with 10% concentration of HCl for the removal of carbonate minerals. Further, the sample was subjected to Soxhlet extraction with 1:4 (wt/wt) CH₃OH: DCM, for 24 hours to remove any remaining bitumen. The carbonate-free oil shale was washed with an excess amount of water for the removal of any remaining HCl. Then the sample was dried in a hot air oven for 24 hours at 105°C. In the next acid leaching step, the sample was subjected to 5% HNO₃ at room temperature for 2 hours for the removal of sulfur minerals. Again, the sample was washed with an excess amount of warm water to remove any residual HNO₃, and then dried in a hot air oven for 24 hours at 105°C. In the third leaching step, concentrated HF was used to remove silica minerals from the samples at room temperature for 48 hours. At the end of this step, the sample contains only impure kerogen. The impure kerogen was washed with an excess amount of warm water and dried in a hot air oven for 24 hours at 105°C. For the removal of any residual bitumen and acids, the dried impure kerogen was subjected to Soxhlet extraction with 1:4 CH₃OH: DCM solvent for 24 hours followed by oven drying for 24 hours at 105°C.

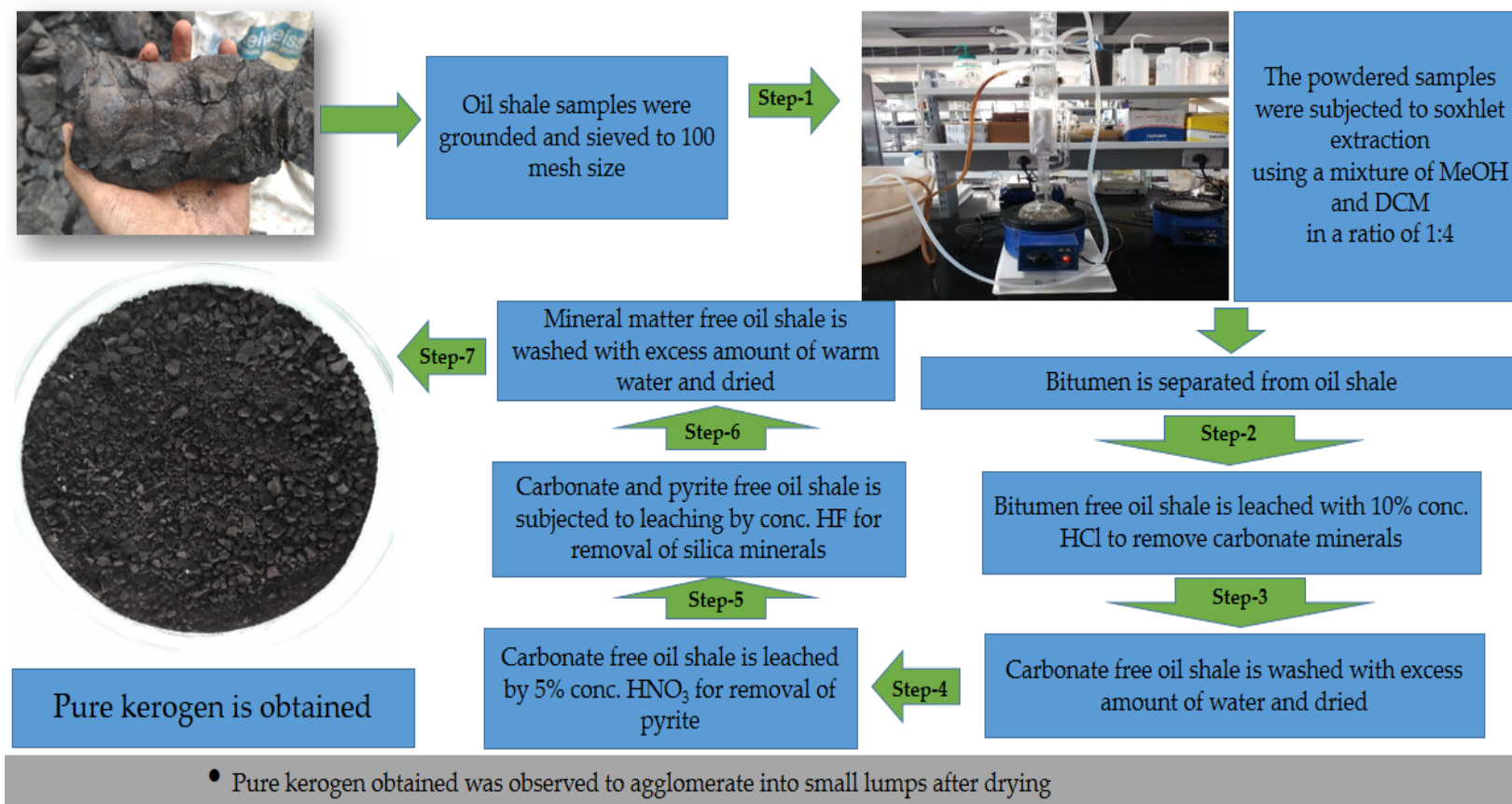


Fig 2.2. Schematic representation of step-by-step demineralization process for extraction of kerogen from oil shale sample.

2.3. Proximate and ultimate analyses

The ultimate analysis (Carbon (C), Hydrogen (H), Nitrogen (N), and Sulfur (S)) of oil shale and kerogen samples was performed using a Eurovector EA3000 Elemental Analyzer under linear calibration according to the ASTM D5373-02 method[147]. The percentage of oxygen was calculated by difference. The proximate analyses were carried out according to ASTM D 3173, 3174, and 3175 methods[148-150] corresponding to moisture content (MC), ash content (AC), and volatile matter (VM) respectively in triplicate, and the average values with standard deviations are reported. For moisture content, initially the crucibles were cleaned with water and acetone. They were then dried in an air-dry oven for 1 hour at 60 °C. The dry weight of the crucibles was recorded and the samples weighing 2 g each were introduced into the crucible and their weight was observed. Four such sets were prepared for each mesh size and were kept for drying in an air-dry oven for 24 hours at 105 °C and the moisture loss was observed every 4 hours. The mean of all readings was calculated to obtain the percentage of moisture content. For ash content was calculated by two methods. One, by heating the samples in a muffle furnace for 5 hours from room temperature to 575 °C and again by preheating the muffle furnace to 575 °C for 5 hours and inserting the sample into the furnace and heating at 575 °C for a time period of 30 minutes. The final weight of the samples was observed and the mean of the difference of initial and final weight of sample were calculated to obtain the percentage of ash content. For volatile matter test the furnace was preheated up to 900 °C and the samples were inserted into the furnace for a time period of 2 minutes and the change in mass was observed and the mean was calculated to find the percentage of volatile matter. The fixed carbon (FC) was determined by difference[151] ($100 - [MC + VM + AC]$). The proximate and ultimate analyses were carried out in total sample basis.

2.4. Rock-Eval analysis

Rock-Eval analysis was conducted using a Rock-Eval 6 analyser (Vinci technology) for the estimation of total organic carbon (TOC), hydrogen index (HI), oxygen index (OI), and identification of types of kerogen in the oil shale sample. The Rock-Eval analysis was carried out from pyrolysis temperature of 40°C to 600°C at a heating rate of 10°C/min, using sample size of 2-3 g. The obtained values of HI and OI were plotted on the Van-Krevelen diagram[152] (Fig 2.3) to identify the grade or type of the kerogen present.

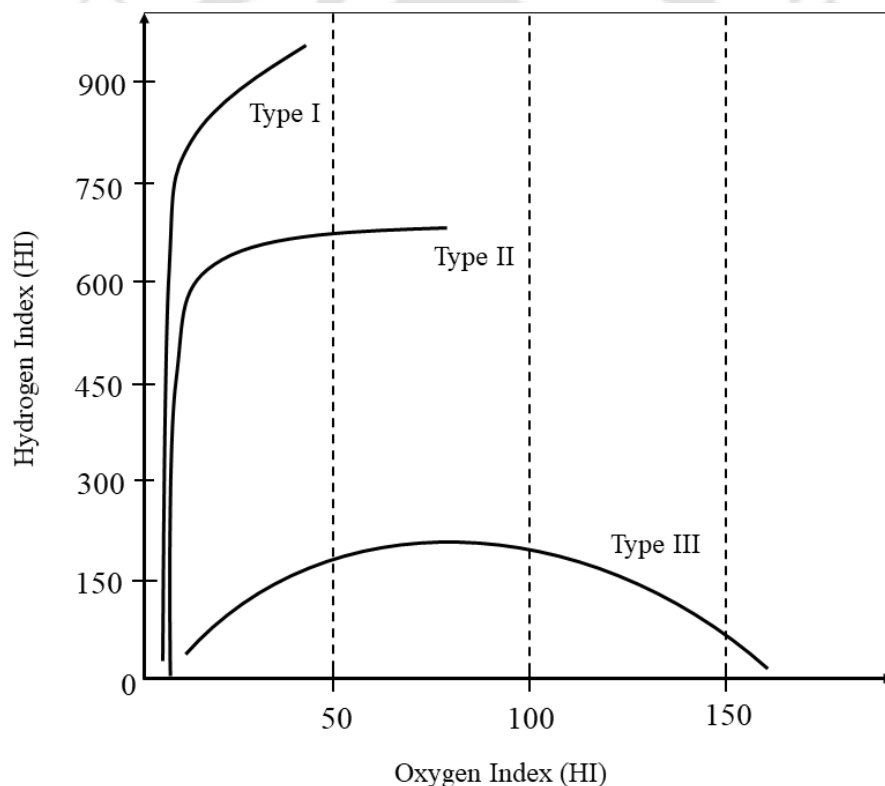


Fig 2.3. Van-Krevelen diagram for identification of the type of kerogen [152].

2.5. Fourier transform infrared spectroscopy (FTIR) analysis

The different functional groups which are present in a carbonaceous material can be identified by Fourier transform infrared spectroscopy (FTIR) analysis. It provides various information on the

composition of a complex mixture of compounds such as hydrocarbon skeleton and the thermal maturity of any carbonaceous compound. FTIR analysis was performed to determine the functional groups present in raw oil shale and extracted kerogen using a Shimadzu IR Affinity FT-IR spectrometer. The powdered samples were binded with KBr powder in the ratio of 1:100 to create pallets for the analysis. The wavenumber (cm^{-1}) was set from 400 cm^{-1} to 4200 cm^{-1} , and the number of scans was set to 30 scans. The pyrolytic oil samples were analyzed using attenuated total reflection (FTIR-ATR) from wavenumber 400 to 4200 cm^{-1} for identification of different functional groups in the oil samples.

2.6. X-ray diffraction (XRD) analysis

The crystal structure and mineral composition of any material can be well-studied by X-ray diffraction analysis. XRD analysis was performed to identify the different mineral matters present in the oil shale sample, and to determine the purity of extracted kerogen using a Bruker D8 Advanced XRD instrument. The 2θ values were set from 5° to 90° . The scanning rate was set at $1^\circ/\text{min}$ with a step size of 0.2° . The obtained XRD data was analyzed by Retvield analysis using MATCH! 3 software.

2.7. Field emission scanning electron microscope & Electron dispersion X-ray spectroscopy (FESEM-EDX) analysis

Field emission scanning electron microscope is used to obtain a magnified image of any sample by focusing a beam of electrons on the sample. It provides ultra-high-resolution image as compared to a standard microscope. The magnification provides a clear image of the pore networks as well carbon skeleton, and the clay and carbonate minerals present in the desired sample. Surface morphology and compositional analysis of raw oil shale, and extracted kerogen was performed using a Sigma Zeiss Siga 300 Field emission scanning electron microscope with energy-dispersive

x-ray spectroscopy (FESEM-EDX). The kerogen, and oil shale samples were pre-dried at 105°C for 24 hours before analysis. The dried samples were coated with double layer gold coating, and magnification was set up to 150KX and scale of 200nm.

2.8. Microscopic analysis

Olympus IX73 inverted microscope with UHLGPS mercury illuminator as fluorescence light source was used to study the surface morphology of the thermal maturation process of kerogen trapped inside oil shale. The samples were placed on a glass slide, and the magnification was set at 10X at a scale of 20µm.

2.9. Gas chromatography analysis

Gas chromatography, and Gas chromatography-mass spectrometry is a method used to analyze the composition of complex chemical mixtures of gaseous and liquid samples by separating each compound based on its boiling point. For analysis of the gaseous compounds, the gas sample is injected into packed and capillary columns for identification of the desired compounds. For the analysis of liquid samples, the liquid samples are diluted with a low boiling point solvent and the mixture is injected into the capillary GC columns of desired use. In the columns the compounds present in the sample are split with respect to their boiling point. In Gas chromatography-mass spectrometry GC-MS analysis the split compounds are separated based on ions and send to an MS detector and the ions are held at the MS detector for identification of the compounds.

2.9.1. Gas chromatography (GC)-TCD/FID

The non-condensable gases were analyzed using a Thermo Fischer Gas chromatograph (Model: Trace 1110). The concentrations of carbon dioxide (CO₂), carbon monoxide (CO), hydrogen (H₂), and methane (CH₄) were determined using a thermal conductivity detector (TCD). A 60/80

Carboxen-1000 (Supelco) column was used with nitrogen as carrier gas (30ml/min). Oven temperature was set at 200°C at a ramp rate of 5°Cmin⁻¹. The injector temperature was maintained at 150°C and the detector temperature was set at 200°C. Hydrocarbon compounds (carbon number C₁-C₅) present in the gases were determined using a flame ionization detector (FID) with the help of a TG-BOND alumina (Thermo Scientific) column. High purity nitrogen was used as carrier gas (4ml/min). The oven temperature was set at 150°C isothermal. The injector and detector temperatures were set at 200°C each. For both TCD and FID, 1 ml of the sample was injected. Gas-mixture standards were used for the identification and determination of the retention time of pyrolytic gases. The areas corresponding to the identified pyrolytic gases were plotted against the standards and the area percentages were calculated for quantification of the gaseous compounds.

2.9.2. Gas chromatography-Simulated Distillation (GC-SimDist)

The carbon number distribution of the pyrolytic oil samples was analyzed by simulated distillation using a TR-SimDist (10m x 0.53mm x 2.65m) column in a Thermo Fischer (Trace 1110) Gas Chromatograph. The simulated distillation was carried out according to the D6352 standard[153][154]. SimDist converts the retention time into boiling points and is used for determining different carbon number range, which can be derived from any oil. SimDist has been previously reported as a reliable method for the identification of different fractions in shale oil[153]. The oven temperature was initially set at 40°C for 2 min, and increased up to 350°C at a rate of 5°Cmin⁻¹, and held at the final temperature for 5 min. High purity nitrogen gas was used as carrier gas (8ml/min). The injector and detectors were maintained at 360 and 350°C respectively. The oil samples were diluted with chromatography grade dichloromethane, and 2µl of the dilute solution was infused into the injector. Two internal hydrocarbon standards (ASTM D3710 and D5307) were used to identify the retention time based on the boiling range of n-paraffins and

aromatics corresponding to gasoline and crude petroleum, which helped in determining the carbon number distribution. The identified compounds were distributed on the basis of their boiling point as light (C_6 - C_{12}), middle (C_7 - C_{20}), and heavy ($>C_{21}$) fractions[153, 155, 156].

2.9.3. Gas chromatography-Mass spectrometry (GC-MS)

Pyrolytic oil samples were analyzed using an Agilent 7000C Triple Stage Quadrupole (TSQ) GC-MS system with a TG-5 MS column (60m x 0.25mm). The oil samples were dissolved in diethyl ether at a dilution concentration of 1:20 (vol/vol%) oil to solvent ratio. The injector and detector temperature were set at 300°C and 310°C respectively. The oven temperature range was set from 40°C to 310°C at a heating rate of 2.25°C/min.

2.10. Nuclear magnetic resonance (NMR) analysis

NMR analysis is used for determination of the carbon and hydrogen content within the pyrolytic shale oil and solvent extracted bitumen. It is used for identification of saturates, aromatics, asphaltenes and resins, present in the oil and bitumen. It is helpful in determining the structural change and in the composition and stability of oil when subjected to higher temperature or catalyst.

1H NMR spectroscopy was performed for identifying the distribution of different functional groups using an Ascend 600 NMR (Make: Bruker), operated at 600 MHz. The liquid samples were dissolved in deuterated chloroform ($CDCl_3$) and the spectra were obtained at 19°C, with number of scans set to 100. The quantification of the compounds was accomplished by using various correlations (Eq 2.1 to 2.11) provided in literature[63, 64, 156, 157].

The data obtained from NMR analysis of liquid samples can be utilized to calculate various properties of the samples. Meyer et al. [158] reported a procedure to broadly classified NMR spectra in aromatic, aliphatic and olefin compounds.

$$\text{Aromatic vol. \%} = \frac{\left(A + \frac{C}{3}\right) 0.97 \times 10^2}{\left(A + \frac{C}{3}\right) 0.97 + \left(D - 2B + \frac{E}{2} + \frac{F}{3}\right) 1.02 + 3.33B} \quad (2.1)$$

$$\text{Paraffin vol. \%} = \frac{\left(D - 2B + \frac{E}{2} + \frac{F}{3}\right) 1.02 \times 10^2}{\left(A + \frac{C}{3}\right) 0.97 + \left(D - 2B + \frac{E}{2} + \frac{F}{3}\right) 1.02 + 3.33B} \quad (2.2)$$

$$\text{Olefins vol. \%} = \frac{3.33B \times 10^2}{\left(A + \frac{C}{3}\right) 0.97 + \left(D - 2B + \frac{E}{2} + \frac{F}{3}\right) 1.02 + 3.33B} \quad (2.3)$$

$$\text{Isoparaffin index} = \frac{CH_3}{CH_2} = A_{(0.5-1)} / A_{(1-1.5)} \quad (2.4)$$

$$\text{Research octane number (RON)} = 80.2 + 8.9 \text{ Isoparaffin index} + 0.107 \text{ aromatic (vol\%)} \quad (2.5)$$

Here, A, B, C, D, E and F are integral intensity assignment of Proton (^1H) assignment at chemical shifts 0.5-1.5, 1.5-3, 2-3-4, 4-6.5, 6.5-7.5, and 7.5-10 respectively.

Further Kumar et al.[10] provided the correlations (eq.2.1-2.6) to characterize the samples in terms of total relative carbon distribution (T_c), total group molecular weight of aromatic compounds (T_w), average alkyl chain length linked to an aromatic ring (n) and substituted aromatic ring carbons (A_s).

$$T_c = A + \frac{B}{2} + \frac{C}{3} + \frac{D}{1.25} + \frac{E}{2} + \frac{F}{2} + A_s + A_b \quad (2.6)$$

$$T_w = 13(A + B) + 9C + \frac{13.25D}{1.25} + 7E + 5F + 12 \times 0.71I_d \quad (2.7)$$

$$A_w = 13A + n \times 7B + 5C + 12A_s + 1A_b \quad (2.8)$$

$$n = \frac{B}{2} + \frac{D}{2} + \left(\frac{\frac{F}{2}}{\frac{B}{2}}\right) \quad (2.9)$$

$$A_s = \frac{B}{2} + \frac{C}{3} \quad (2.10)$$

$$A_b = 0.71I_d \quad (2.11)$$

Here, A, B, C, D, E, F and I_d are integral intensity assignment of Proton (¹H) assignment at chemical shifts and 7.5-10, 6.5-7.5, 4-6.5, 2-3-4, 1.5-3, 1-1.5, and 0.5-1 respectively.

2.11. Thermogravimetric analysis-Differential thermogravimetry (TGA-DTG)

Thermogravimetric analysis and Differential thermogravimetry (TGA-DTG) is used for investigating the thermal degradation of any organic material under the influence of heat either in presence of air or in an inert atmosphere. Thermogravimetric analysis coupled with Fourier transform infrared spectroscopy (TGA-FTIR) is used for real time analysis of compounds evolved during thermal degradation of any organic material. High-Pressure thermogravimetric analyser (HP-TGA) is used for the investigation of the thermogravimetric degradation of the oil shale at elevated pressure, and in an inert environment.

2.11.1. Thermogravimetric analysis (TG-DTG)

Thermogravimetric analysis (TGA) was performed using a NETZCH TG 209F1 Libra analyser (Germany). Oil shale samples (about 8-10mg) of 100 mesh size (150 microns) were heated from 30 to 1000 °C, at four different heating rates of 10, 20, 30 and 50 °C/min respectively. Nitrogen was used as purge and balance gas at flow rate of 40 ml/min and 20 ml/min respectively. The samples were held at maximum temperature for 10 minutes.

2.11.2. Thermogravimetry-Fourier transform infrared spectroscopy (TG-FTIR)

TG-FTIR analysis was conducted using a Perkin Elmer TGA 4000 coupled with a Perkin Elmer Frontier FT-IR Spectrometer. Oil shale and kerogen samples of 150 microns (weight 7-8 mg) were heated at heating rates of 10, 20, 30, and 50 °C/min from 30 to 800°C under inert atmosphere by nitrogen (N₂) as purge (40 ml/min) and balance (20 ml/min) gas and the samples were held at maximum temperature for 10 minutes. The TGA experiments were triplicated to confirm repeatability. The produced gases from the TGA were carried to the coupled FTIR through a heated

transfer line maintained at 250°C to prevent any condensation of the evolved vapours and analyzed from wave number 450 cm⁻¹ to 4200 cm⁻¹.

2.11.3. High-Pressure thermogravimetric analysis (HPTGA)

High-pressure thermogravimetric analysis (HP-TGA) was carried out using an HP-1100 high-pressure thermogravimetric analyzer (Linseis, Germany). Initially, blank runs were conducted prior to experiments at multiple heating rates and pressure, for calibration of temperature reading and buoyancy effect to stabilize the balance and to confirm reproducibility. Each sample of about 18-20 mg of 150 microns size was heated from 30 to 900 °C, at four different heating rates of 5, 10, 15, and 20 °C/min. The operating pressure was set at 5, 10, 20, and 30 bar. Constant pressure was maintained throughout the experiment using nitrogen as a purge and balance rate of 100 ml/min and 200 ml/min respectively. The samples were then held at maximum temperature for 10 minutes.

2.12. Lab-scale pyrolysis experiments

The process of heating a material in the absence of air or in an inert atmosphere, to produce oil, gas and char is called pyrolysis. Pyrolysis process are generally classified into two categories based on heating rate viz. non-isothermal pyrolysis and isothermal pyrolysis. Non-isothermal pyrolysis is further classified into fast and slow pyrolysis. Based on the type of environment and sample pretreatment, pyrolysis process can be further classified into catalytic pyrolysis, High-pressure pyrolysis, and hydrous pyrolysis.

In the present study the oil shale samples were subjected to non-isothermal pyrolysis under semi-batch condition for benchmarking the yield of hydrocarbons and to identify influential pyrolysis parameters on yield and composition. The oil shale samples were then subjected to non-isothermal

semi-batch high pressure lab-scale pyrolysis experiments. The effect of pressure was also studied in the presence of water under isothermal batch condition, and finally the oil shale samples were subjected to co-pyrolysis experiments with lignocellulosic biomass under non-isothermal, semi batch condition.

2.12.1. Semi-batch pyrolysis experiments

The semi-batch lab scale pyrolysis experiments of the oil shale samples were carried out using a fixed bed semi-batch alloy reactor (1-liter capacity) of 3 inch internal diameter (ID) and 9 inch height. heated by an electric furnace controlled by a PID controller. The schematic diagram of the lab scale pyrolysis setup is shown in Fig 2.4 (Photograph is in shown in Fig 2.8). The experimental matrix of the lab-scale pyrolysis experiments was formulated using Design of Experiments (DOE) software (Design Expert 11) and the process parameters were optimized using Response Surface Methodology (RSM) for identification of significant pyrolysis parameters during oil shale pyrolysis. Three parameters viz. pyrolysis temperature, heating rate, and particle size were considered to record five responses viz. mass loss, oil yield, gas yield, aqueous phase, and char yield. The pyrolysis temperatures range was considered from 450 °C to 650 °C, at heating rate ranging from 5 °C/min to 20 °C/min. The oil shale particle size was selected in the range of 0.150 mm to 10mm size. For each experiment 50 g sample was used. Nitrogen (N₂) gas was used as purge gas at a flow rate of 100 ml/min. The produced vapors were passed through two inline spiral condensers connected in series and maintained at 4°C/min using a circulating water chiller. The condensed oil products were collected in a round bottom conical flask immersed in a chiller water bath, and the uncondensed vapors were collected in Tedlar bags.

Response Surface Methodology (RSM) has been established as a reliable and simplified technique to maximize or minimize the yield of different pyrolytic products [22, 159, 160]. RSM provides

an effective one-on-one factor to parameter study for testing of multiple process parameters because of its requirement of a smaller data set of experiments [161, 162]. Because of its structures' nature, RSM has been reported to provide more accurate sensitive analysis and interactive effect between two components [163]. For the purpose of optimization, central composite design (CCD) was used as the optimization method. CCD method is widely used to fit empirical polynomial model based on multiple groups of design, fractional factorial points, axial points and central points [22, 164]. The total number of experiments required is determined by the equation $2^n + 2n + c$, where “n” is the number of parameters and “c” is the number of center points. Central composite design (CCD) model suggested twenty experiments with six center points.

The percentage of products formed were calculated using the formulas stated below,

Mass conversion (wt %) = initial sample weight – weight of spent shale

Oil yield (wt %) = $\frac{\text{Weight of oil produced}}{\text{Initial sample weight} - \text{weight of spent shale}}$

Aqueous phase (wt %) = water diffused in oil obtained by gravity separation method

Gas yield (wt %) = Mass conversion – oil yield – aqueous phase

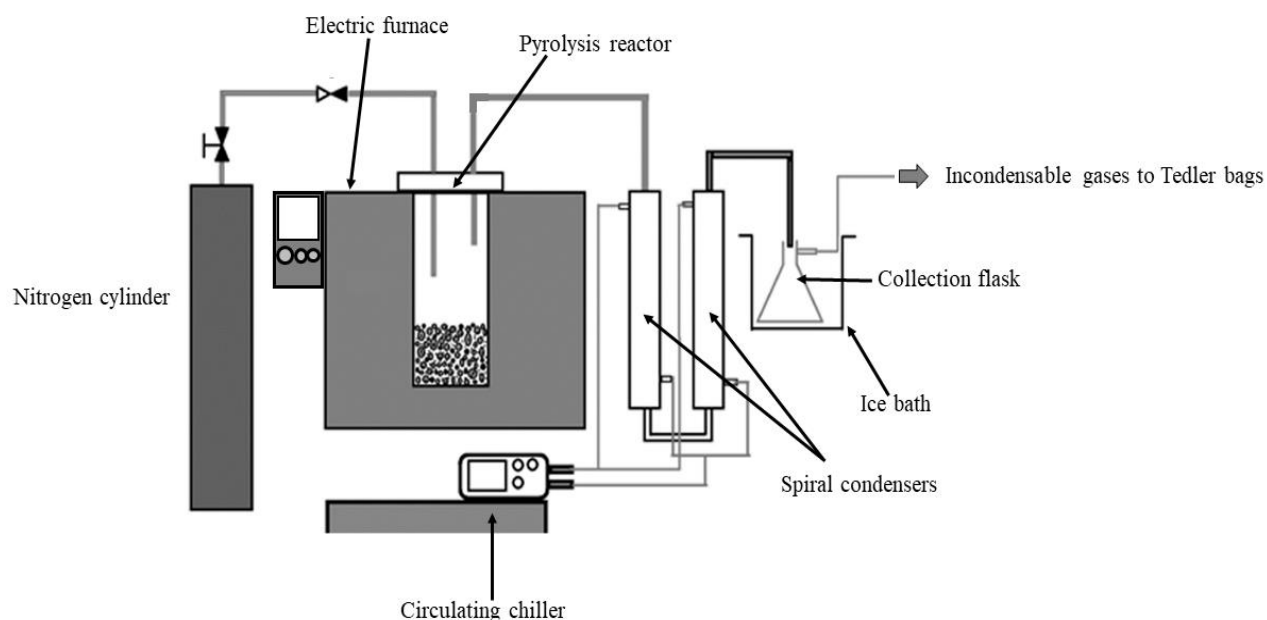


Fig 2.4. Schematic diagram of lab-scale pyrolysis setup.

2.12.2. High-pressure pyrolysis

Pyrolysis of oil shale under influence of high pressure was conducted in a lab-scale pyrolysis setup developed using a Swagelok semi-batch tubular reactor (SS316) of 350ml capacity of dimension 2-inch x 7 inch (ID x Length), heated externally by a tubular electric furnace, controlled by a PID controller. The schematic diagram of the High-pressure pyrolysis setup is portrayed in Fig 2.5, and the photograph of the assembly is shown in Fig. 2.9. The desired pressure in the reactor was maintained using nitrogen as purge gas. A backpressure regulator was used to control and regulate the pressure inside the reactor. Based on TG data, six pyrolysis temperatures (350, 450, 500, 550, 600, and 650°C) and four isobaric pressure (5, 10, 20, and 30 bar) values were selected. All the experiments were performed at three heating rates of 5, 10, and 20 °Cmin⁻¹ and subsequently held at the final temperature for 2 hours. Approximately 30 g sample was used for each run. The produced gases and oil products were passed through a spiral condenser to condense the vapor products. Cooling water mixed with ethylene glycol (1:20 vol/vol) was circulated through the

condenser at a temperature below 4°C from a circulating water bath. The condenser was connected to a conical flask to collect the condensed products. The condensed products were subjected to gravity separation for separation of the aqueous phase. The non-condensable gases were collected using Tedlar bags periodically (for each heating rate) at different reactor temperature values (300, 350, 400, 450, 500, 550, 600, and 650°C) during the pyrolysis process.

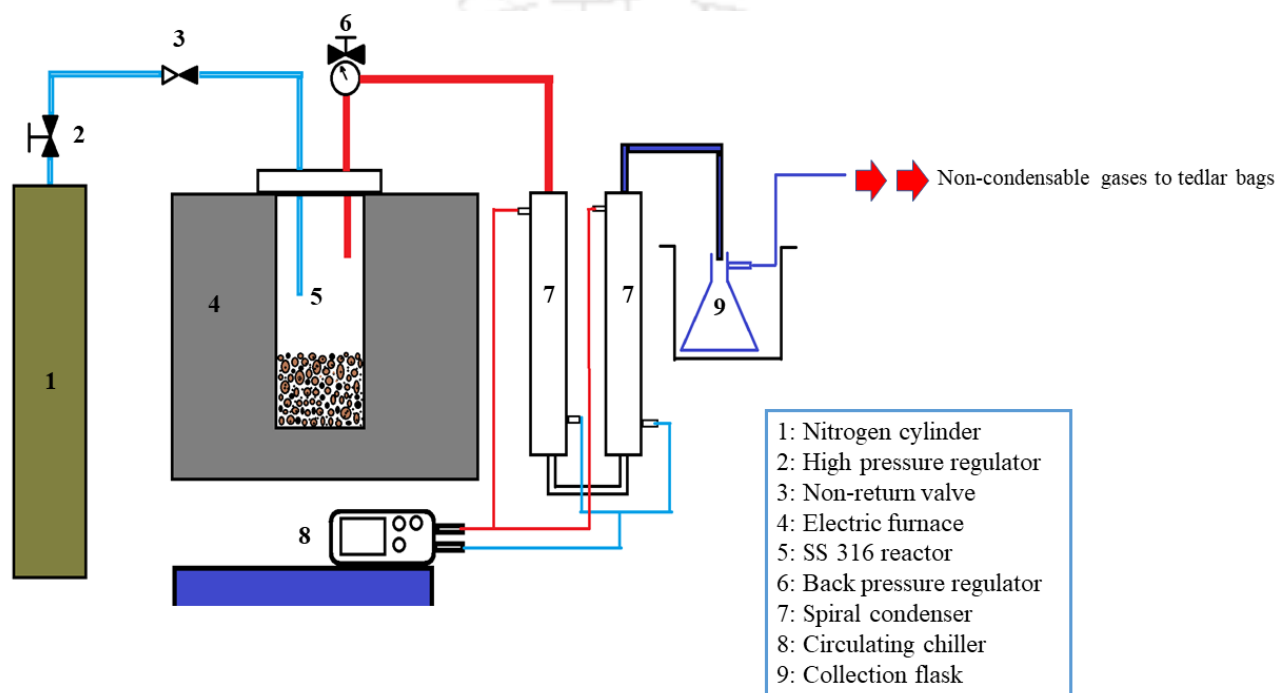


Fig 2.5. Schematic diagram of high-pressure lab scale pyrolysis setup.

2.12.3. Soaking and hydrous pyrolysis

The lab-scale pyrolysis experiments were performed using two different methods. In one method 30g of powdered oil shale samples (100 mesh) were pre-soaked in 50 ml deionized water (DI) and 50 ml brine solution separately for a period of 1, 2, 3, and 4 weeks. 30 g sample was used for each pyrolysis temperature and soaking time. The brine solution was prepared by mixing NaCl and DI water in a ratio of 1:10. The concentration of brine solution was considered to reproduce the

concentration of a high salinity underground aquifer[165, 166]. The NaCl used in the brine water was of ACS grade and procured from Merck life sciences.

The soaked oil shale samples were then subjected to vacuum filtration for removal of any water on the surface and weighed to check for change in weight of the soaked samples. The soaked oil shale samples were then pyrolysed in a high-pressure stainless steel (SS316) tubular reactor (make: Swagelok; capacity 350 ml) at isothermal pyrolysis temperature of 300, 350, and 400°C for duration of 72 hours at a maximum isobaric pressure of 90 bar. The pressure in the reactor was monitored using a Swagelok back-pressure regulator. Before heating, the reactors were purged with nitrogen (N₂). The pressure was built up inside the reactor using N₂ as purge gas and also by the autonomous pressure generated by the vaporization of water. In the second method, the oil shale samples (30g) were mixed with 50 ml of DI water and 50 ml of brine solution separately inside the Swagelok high-pressure tubular reactor. The obtained oil shale slurry was subjected to isothermal pyrolysis at 300, 350, and 400°C, respectively for a duration of 72 hours and at maximum autonomous pressure of 125 bar. Same quantity of oil shale sample (30 g) was used for each hydrous pyrolysis experiment to maintain homogeneity throughout the study. The Soaking and hydrous pyrolysis experiments were carried out in a novel tubular electric furnace, controlled by a PID controller. The furnace was heated at a heating rate of 30°Cmin⁻¹ till final pyrolysis temperature was reached and was held at the final pyrolysis temperature isothermally for 72 hours. The schematic diagram of the pyrolysis setups used for Soaking and hydrous pyrolysis are portrayed in Fig 1 (a-b). After pyrolysis process the high-pressure reactors were allowed to cool down inside the furnace. After cooldown, the gas samples were collected in Tedlar bags through the release valve before opening the reactors. The liquid (oil and aqueous phase) and solid samples were transferred into separate vessels from the reactor. The oil was separated from the aqueous

phase by gravity separation method. The pyrolysis experiments were triplicated to confirm repeatability and the mean values have been reported.

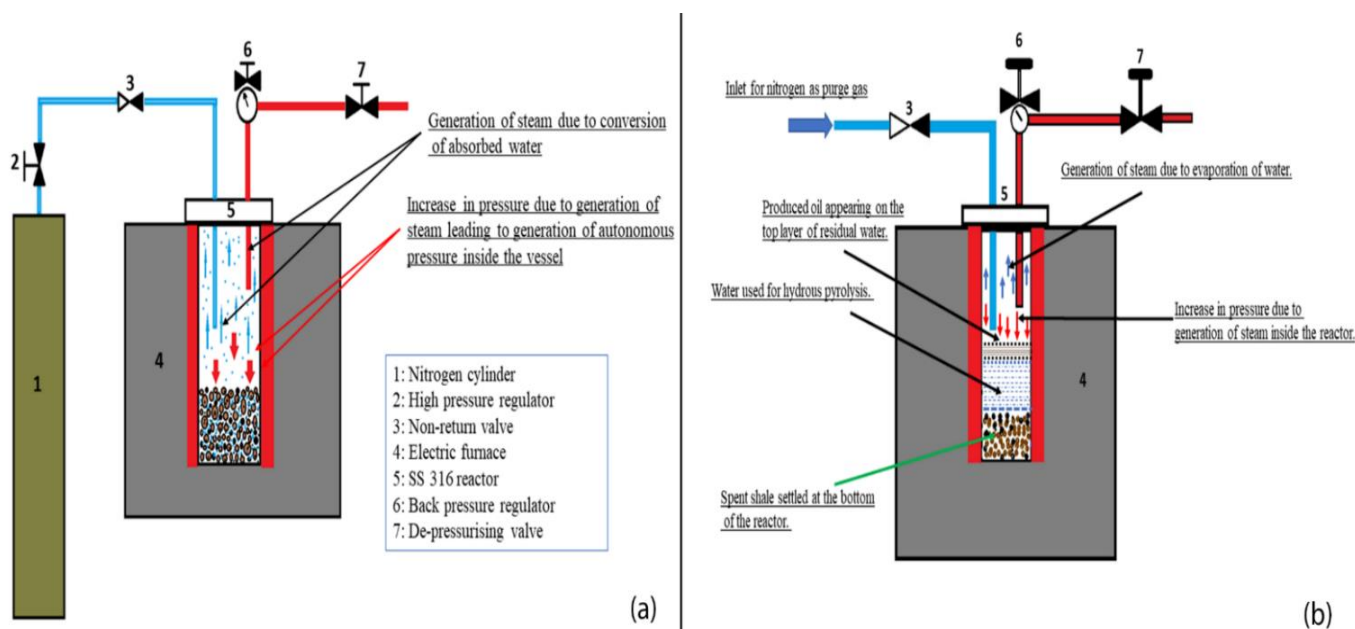


Fig 2.6. (a) Schematic diagram of lab-scale soaking, and (b) hydrous pyrolysis experiments.

2.12.4. Co-pyrolysis of oil shale with lignocellulosic biomass

The targeted co-pyrolysis experiments were performed using a semi-batch pyrolysis reactor (Fig 2.4 and Fig 2.8). The experiment matrix was formulated using Design Expert 11. In the present study, central composite design (CCD) was used as the optimization method. CCD method is widely used to fit empirical polynomial model based on multiple groups of design, fractional factorial points, axial points and central points [22, 164]. The total number of experiments required is determined by the equation $2^n + 2n + c$, where “n” is the number of parameters and “c” is the number of center points. For the present study, three parameters were considered viz. blending ratio, heating rate, and temperature, and five responses viz. mass loss, oil yield, gas yield, aqueous yield, and char yield were recorded. Central composite design (CCD) model suggested twenty

experiments with six center points. The OS:RSS sample blending ratio was considered in the range of 1:2 to 2:1. The heating rate was set in the range from 5°C/min to 20°C/min and final pyrolysis temperatures from 450°C to 600°C. Mixture sample (~50 g) was used to carry out each pyrolysis experiment in an inert environment produced by a continuous flow of nitrogen at 100ml min⁻¹, and held isothermally at final temperature for 2 hours. The produced vapors were passed through two spiral condensers connected in series, and the oil inside the condensers was washed out using dichloromethane. The emulsion of oil (with dissolved solvent) and aqueous phase were subjected to gravity separation for removal of the aqueous phase. The collected oil dissolved in solvent [151] was subjected to rotavapor for separation. Finally, the solvent and aqueous phase-free oil was collected and characterized. The produced gases during pyrolysis experiments at pyrolysis reactor temperatures of 300, 350, 450, 500, 550°C and at different heating rates were collected in Tedlar bags after passing through the series of condensers.

2.12.5. Catalytic pyrolysis of oil shale sample

The oil shale samples were subjected to catalytic pyrolysis with an industrial grade zeolite (Ammonium ZSM-5, purchased from Alfa Aesar, Thermo Fisher Scientific) to investigate the industrial usage and upgradability of the produced pyrolytic oil and gases. The catalytic pyrolysis was carried out in a novel two stage catalytic pyrolysis setup consisting of individual sample and catalysis reactor (Fig 2.7. (a)-(b) and Fig. 2.10). Two pyrolysis to feed ratio was selected as 1:50 (wt:wt) and 1:25 (wt:wt), and the catalytic reactor was maintained isothermally at 500°C and 550°C. 50 g oil shale sample of particle size 150 micron was heated in the sample reactor to 600°C at 10°C/min and held at 600°C for a duration of 2 hours. The oil shale sample of size 0.150mm was considered for all the pyrolysis experiments. The produced vapors from the sample reactor was carried into the catalytic reactor by N₂ as carrier gas at a flow rate of 200ml/min and passed

through the catalyst bed. The cracked vapors were then carried out of the reactor by the carrier gas stream into a spiral graham condenser which was maintained at 4°C by circulating cooling water. The condensed products were collected in a volumetric flask submerged in an ice bath, and the uncondensed vapors were collected in a Tedlar bag.

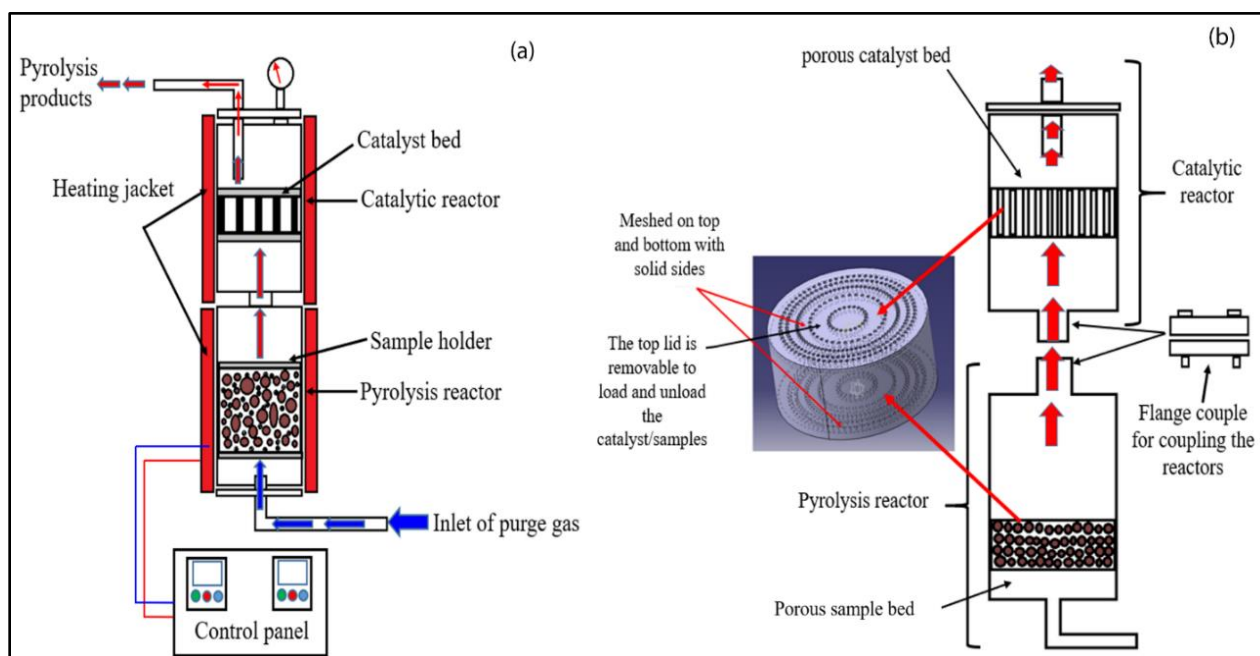


Fig 2.7. (a) Schematic of novel two-stage catalytic pyrolysis reactor unit, and (b) assembly of the sample and catalytic reactors.

2.13. Physicochemical properties of fuel

2.13.1. Calorific value

The calorific value of the oil sample is defined as the amount of heat produced when an unit mass of the sample is burned in excess supply of oxygen.

An Oxygen bomb calorimeter (make: Toshniwal, with Parr 1341 plain jacket bomb) was used for determination of the calorific values of the pyrolytic oil samples. The calorific values were determined by the ASTM D 4809 [167] method. 0.5 to 1 g sample was placed in the sample holder, and burned inside the seal bomb or container after being pressurized by pure oxygen gas to a

pressure of 20 bar. The heat capacity of the bomb calorimeter was determined by testing the calorimeter with a sample of known calorific value.

2.13.2. Flash point and fire point

The flash point of a particular fuel may be defined as the temperature at which the fuel produces enough vapors to ignite and produce a white flash when a flame is passed over it. The fire point of a particular fuel may be defined as the temperature at which the oil sample starts burning continuously for a duration of 5 seconds. The flash point and fire point were determined according to the ASTM D92 [168] method using the Cleveland open cup apparatus.

2.13.3. Pour point and cloud point

Pour point of a fuel is defined as the lowest temperature at which the liquid stops to flow. Cloud point may be defined as the temperature at which the liquid hydrocarbons undergo crystallization to form wax and has a cloudy appearance. The pour point and cloud point were determined by the ASTM D97 [169] method.

2.13.4. Carbon residue test

The carbon residue in a fuel may be defined as the tendency of the fuel to produce carbon deposits when heated to high temperature in an inert environment. The carbon residue test was performed by following the ASTM D189 [170] method. 2 gm oil sample were placed in a porcelain crucible with a lid on. The crucible was then placed in a muffle furnace and heated to 800°C for a duration of 5 min. The residual carbon was observed to be in the form of coke and weighed to determine the carbon residue.



Fig 2.8. Experimental setup for pyrolysis reactor assembly, with condenser, and circulating chiller used for standard pyrolysis and co-pyrolysis experiments at atmospheric pressure.

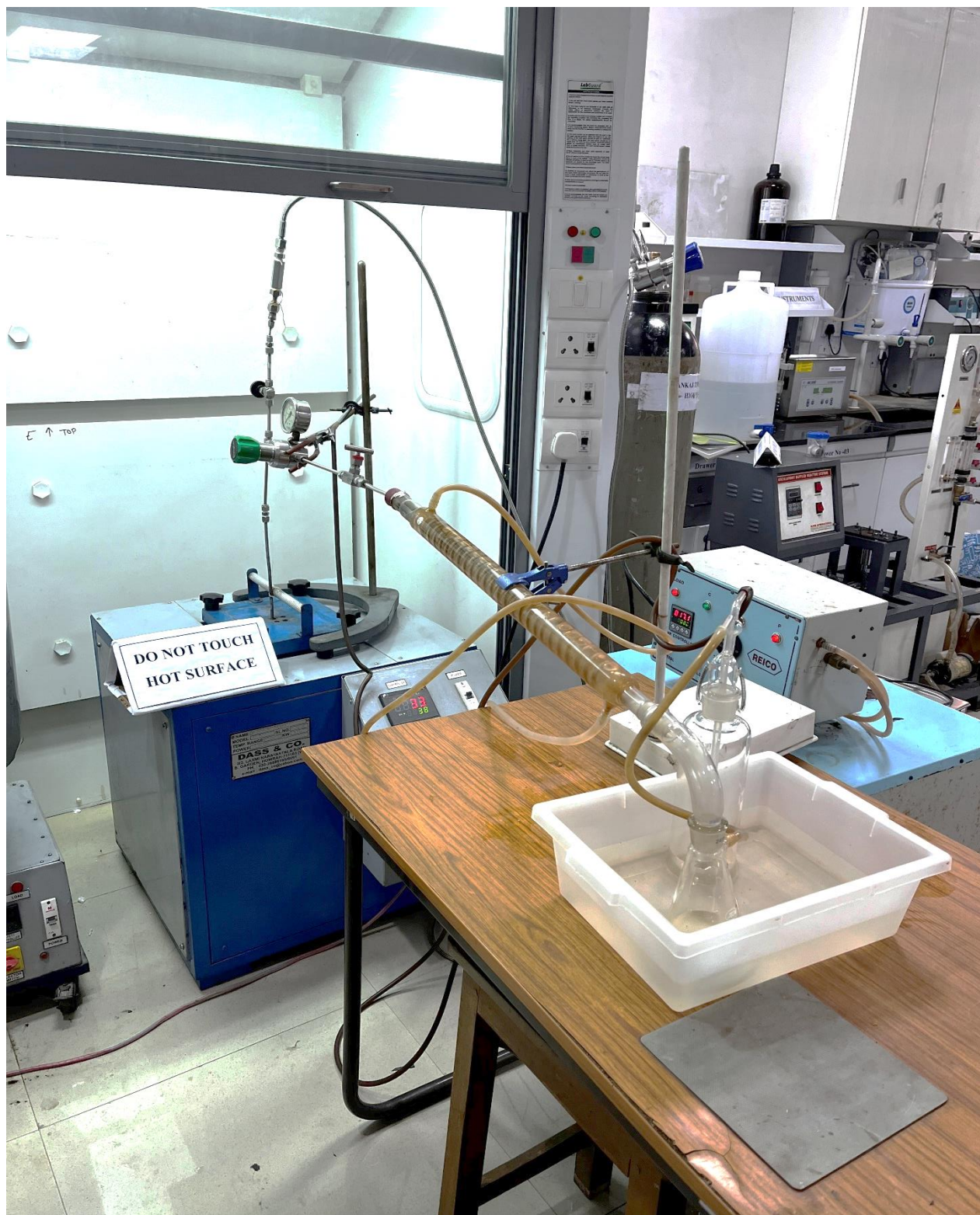


Fig 2.9. Experimental setup for high-pressure pyrolysis reactor assembly, with back-pressure regulator, condenser, and circulating chiller used for semi-batch high pressure pyrolysis experiments and soaking and hydrous pyrolysis experiments.



Fig 2.10. Experimental setup for catalytic pyrolysis reactor assembly, with ondenser, and circulating chiller used for semi-batch catalytic pyrolysis experiments.

2.14. Kinetic study

During pyrolysis of oil shale, the organic matter (kerogen) gets converted into oil, gas, and char. This conversion is caused by breaking of bonds and occurrence of multiple parallel reactions [27].



The mechanism of oil shale pyrolysis can be studied by non-isothermal thermogravimetric gravimetric and differential thermogravimetric (TG-DTG) analysis. Non-isothermal heating shows the thermal degradation behavior at different temperatures and, the interaction between heating rate and the reaction mechanism. The non-isothermal heating also removes the errors produced by the thermal induction period and allowing a rapid scan over a certain temperature range[38]. Kinetic study of pyrolysis processes based on TG data has been extensively discussed in literature[27, 28, 133, 171]. In this study, for the estimation of pyrolysis kinetic parameters, the pyrolysis zone for organic matter has been identified from TG data.

2.14.1. Determination of apparent activation energy value

Kinetic study deals with parameterization and measurement of process rates. During a particular chemical process, the process rate is governed by temperature (T), extent of conversion (α), and pressure (P)[38] as,

$$\frac{d\alpha}{dt} = k(T)f(\alpha)h(P) \quad (2.12)$$

In consideration of the above equation, pressure may have a marked effect on the thermally stimulated process kinetics. Burnham[51] stated that the function $h(P)$ can be fundamental or empirical-based. Separating the effect of pressure from reaction kinetics is an approximation and

is not always true or valid. In the case of hydrocarbon cracking and degradation, the effect of pressure is not truly separable, and any change in pressure is reflected in a relative amount of initiation, propagation, and termination reactions which leads to change in global activation energy values. According to the ICTAC guidelines, for thermal degradation reaction involving pressure dependency, the effect of the pressure is considered to be constant ($h(P) = \text{constant}$) throughout the entire reaction if an excess amount of gaseous reactants are supplied in gas-solid reaction or by effectively removing reactive gaseous products[38]. In the present study, the reactive gaseous products were continuously removed from the system by the purge gas. The influence of pressure during pyrolysis was reflected in the delay of volatilization of organic matter degradation, increase in activation energy values, the occurrence of intermediate reaction models, and product distribution and composition.

For non-isothermal reaction, on the assumption that the temperature dependence can be calculated by the Arrhenius equation[38, 172], the rate of conversion can be calculated as,

$$\beta \frac{d\alpha}{dT} = A \exp\left(\frac{-E_a}{RT}\right) f(\alpha) \quad (2.13)$$

Where, β is the heating rate, $d\alpha/dT$ is the conversion rate of reaction, $f(\alpha)$ is the reaction model, E_a is the activation energy and A is the pre-exponential factor.

Different forms of isoconversional methods; differential (Friedman[173]) and integral ((Flynn Wall Ozawa (FWO[174, 175]), Kissinger Akahira Sunnose (KAS[176]), and Starink method [177]) have been formulated based on different assumptions on the standard isoconversional equation. According to the guidelines provided by ICTAC[38], among the three widely used integral isoconversional methods (FWO, KAS, and Starink), the Starink method provides the most reliable activation energy values. The accuracy and reliability of the kinetic data can be increased

by using non-linear integral methods such as the advanced isoconversional method (AIC)[154, 178, 179]. Therefore, in the present study the apparent activation energy values have been calculated using Friedman, Starink, and AIC method and the error percentage for each method has been discussed. The general equations of the isoconversional methods are tabulated in Table 2.1. The accuracy of the obtained kinetic parameters can be predicted by comparing simulated conversion curves with the experimental curves[38]. In this study AIC method showed the highest average R^2 value during fitting of experimental vs simulated conversion plots [Section 3.2.3]. The effect of pressure can be observed in the change occurring in E_α , A_α values and in the occurrence of different $(f(\alpha))_\alpha$ models throughout the pyrolysis process. The approximations used in formulation of the models are summarized in Table 2.1.

Table 2.1. Different Isoconversional methods considered for kinetic analysis [151].

Type	Isoconversional Methods	Expressions	Approach	Plot for determination of activation energy
Differential	Friedman	$\ln\left(\frac{d\alpha}{dt}\right) = \ln\left(\beta \frac{d\alpha}{dT_\alpha}\right)$ $= \ln[Af(\alpha)]$ $- \frac{E_a}{RT_\alpha}$	Application of isoconversional principle to $\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha)$	$\ln\left(\beta \frac{d\alpha}{dT}\right)$ vs $\frac{1}{T}$ [173]
Linear Integral	Starink method	$\ln \frac{\beta_i}{T_{\alpha,i}^2} = \ln \left(\frac{AR}{E_a g(\alpha)} \right) - \frac{E_a}{RT_\alpha}$	$\ln \left(\frac{\beta_i}{T_{\alpha,i}^B} \right) = \text{constant}$ $- C \left(\frac{E_a}{RT_\alpha} \right)$ Where, $B = 1.92$, $C = 1.0008$	$\ln \frac{\beta}{T^{1.92}}$ vs $\frac{1}{T}$ [177]
Non-linear integral	Advanced Isoconversional method	$\Phi(E_a) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{J[E_a, T_i(t_a)]}{J[E_a, T_j(t_a)]} = 0$	It is a distributed activation energy model where activation energy values are calculated by minimization of the function $\Phi(E_a)$.	[154, 178, 179]

Table 2.2. Algebraic expressions of the functions of the most common reaction mechanism [45].

Mechanism	$f(\alpha)$	$g(\alpha)$
First Order, F1	$1-\alpha$	$-\ln(1-\alpha)$
Second Order, F2	$(1-\alpha)^2$	$(1-\alpha)^{-1}$
1-D Diffusion, D1	$1/(2\alpha)$	α^2
2-D Diffusion, D2	$1/[-\ln(1-\alpha)]$	$[(1-\alpha)\ln(1-\alpha)]+\alpha$
3-D Diffusion, D3	$3/2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	$[1-(1-\alpha)^{1/3}]^2$
Contraction Area, R2	$2(1-\alpha)^{1/2}$	$[1-\ln(1-\alpha)]^{1/2}$
Contraction Volume, R3	$3(1-\alpha)^{1/3}$	$[1-\ln(1-\alpha)]^{1/3}$
Power Law, P2	$2\alpha^{1/2}$	$\alpha^{1/2}$
Power Law, P3	$3\alpha^{2/3}$	$\alpha^{1/3}$
Power Law, P4	$4\alpha^{3/4}$	$\alpha^{1/4}$
Power Law, P2/3	$(2/3)\alpha^{-1/2}$	$\alpha^{3/2}$
Avrami Eroffev, A2	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$-\ln(1-\alpha)^{1/2}$
Avrami Eroffev, A3	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$-\ln(1-\alpha)^{1/3}$
Avrami Eroffev, A4	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$-\ln(1-\alpha)^{1/4}$

2.14.2. Determination of reaction model by Criado master plot

After determination of the apparent activation energies for constant values of conversion, the model of the reaction can be determined with the help of Criado Master Plot [180-184]. In general, differential-integral Criado master plot or Z-alpha master plot is used [180]. The generalized equation for Criado master plot is presented below [183, 184],

$$\frac{d\alpha}{d\theta} = \frac{d\alpha}{dt} \exp\left(\frac{-E}{RT}\right) \quad (2.14)$$

Where $\frac{d\alpha}{d\theta}$ is the generalized reaction rate. As the activation energy is known, extrapolated experimental data recorded under any heating rate. Eq. (2.15) stands valid for the analysis of any particular data which is independent of the temperature profiles under which they were analyzed.

Taking, $\alpha = 0.5$ as the reference point as, the following are obtained,

by differential method

$$\left(\frac{\frac{d\alpha}{d\theta}}{\left(\frac{d\alpha}{d\theta}\right)_{0.5}}\right) = \frac{f(\alpha)}{f(0.5)} \quad (2.15)$$

by integral method,

$$\left(\frac{\frac{d\alpha}{d\theta}}{\left(\frac{d\alpha}{d\theta}\right)_{0.5}}\right) = \frac{g(\alpha)}{g(0.5)} \quad (2.16)$$

As, $f(0.5)$ & $g(0.5)$ is constant for a certain kinetic model [184], the eq (2.15) and eq (2.16) indicate that, for any given value of α , the reduced generalized equation, $(d\alpha/d\theta)/(d\alpha/d\theta)_{0.5}$ becomes equivalent to $f(\alpha)/f(0.5)$. The differential-integral form of the equation is expressed as,

$$\left(\frac{T}{T_{0.5}}\right)^2 \times \left(\frac{\theta \left(\frac{d\alpha}{d\theta}\right)}{\theta_{0.5} \left(\frac{d\alpha}{d\theta}\right)_{0.5}}\right) = \frac{[f(\alpha)g(\alpha)]}{[f(0.5)g(0.5)]} \quad (2.17)$$

Eq. (2.17) can be expressed as [181],

$$\left(\frac{T}{T_{0.5}}\right)^2 \times \left(\frac{\theta \left(\frac{d\alpha}{d\theta}\right)}{\theta_{0.5} \left(\frac{d\alpha}{d\theta}\right)_{0.5}}\right) = \frac{[f(\alpha)g(\alpha)]}{[f(0.5)g(0.5)]} = \left(\frac{Z(\alpha)}{Z(0.5)}\right) \quad (2.18)$$

Where, $Z(\alpha) = f(\alpha) \times g(\alpha)$

The algebraic expressions of $f(\alpha)$ and $g(\alpha)$ for considered the theoretical reaction models are given in Table 2.2 The point $\alpha = 0.5$ is considered as the reference point because at $\alpha = 0.5$ the standard master plots of each considered kinetic mechanism intersect each other corresponding to value of $(d\alpha/d\theta)/(d\alpha/d\theta)_{0.5} = 1$ [180].

2.14.3. Determination of pre-exponential factor using compensation factor

From the activation energy and the determined reaction model, the pre-exponential factor can be determined using the compensation factor method [38, 39, 172]. The equation of compensation factor is given as,

$$\ln(A(f(\alpha))_\alpha) = \frac{E_\alpha}{RT_\alpha} + \ln\left(\left(\frac{d\alpha}{dt}\right)_\alpha\right) \quad (2.19)$$

The equation can be simplified as,

$$b = \ln(A(f(\alpha))_\alpha) - a \quad (2.20)$$

$$\text{where, } a = \frac{E_\alpha}{RT_\alpha} \text{ and } b = \ln\left(\left(\frac{d\alpha}{dt}\right)_\alpha\right)$$

According to this method the values of activation energy, E_α and $A(f(\alpha))$ at various extents of conversion follows a logarithmic pattern, and compensates one another in every stage of conversion. For each value of α , the values of a and b can be calculated. The values of $\ln(A(f(\alpha))_\alpha)$ can be calculated from the intercept of the plot between b and a following isoconversional

principle. Subsequently, using the model predicted by Criado master plot the values of pre-exponential factor can be determined using the term $\ln(A(f(\alpha))_{\alpha})$.

2.14.4. Reconstruction of thermogravimetric data

The kinetic triplets obtained from different isoconversional models were used for the reconstruction of conversion (α) vs temperature (T) profiles. The formulation of an ordinary differential equation was done with the kinetic triplet obtained and the equation was solved using the ODE45 function in MATLAB 2016a, assuming temperature as an independent variable. The reconstruction methodology was used for each heating rate. The obtained simulated data for α vs T profiles were plotted against the experimental profiles and the linearity of the fitting was estimated using regression analysis.

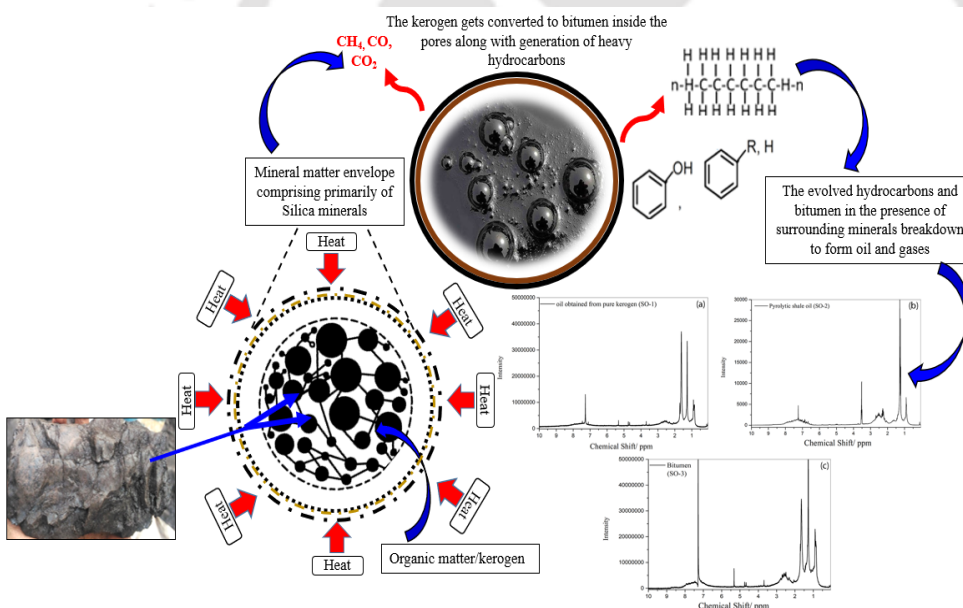
2.15. Conclusive summary

In the present study, the oil shale samples were subjected to physicochemical and thermochemical conversion prior to lab-scale pyrolysis experiments. The degradation zone of the oil shale sample was identified by thermogravimetric analysis, and the identified temperature region was used for designing lab-scale pyrolysis experiments. Different lab-scale pyrolysis experiments were conducted to study the effect of pyrolysis temperature, heating rate, particle size, pyrolysis pressure, presence of water, and co-pyrolysis on product yield and composition. And, the produced products samples were characterized by different standard analytical characterization techniques.

Chapter 3

Detailed characterization, kinetic study and lab-scale pyrolysis of Indian oil shale and extracted kerogen to benchmark its hydrocarbon generation potential

- Oil shale and isolation of kerogen
- Physicochemical characterization
- Thermochemical characterization
- Kinetic study
- Lab-scale pyrolysis



The part of the work from this chapter is published as:

B. Baruah and P. Tiwari, "Compositional and kinetic study of thermal degradation of kerogen using TG-FTIR, NMR, and microscopic study", *AIChE Journal*, 17396, 2022.

B. Baruah, R. Kataki, P. Thakur, and P. Tiwari, "Detailed physicochemical and thermochemical investigation of Upper Assam oil shale," *Journal of Thermal Analysis and Calorimetry*, vol. 138, 2019.

B. Baruah, P. Tiwari, P. Thakur, and R. Kataki, "TGA-FTIR analysis of Upper Assam oil shale, optimization of lab-scale pyrolysis process parameters using RSM," *Journal of Analytical and Applied Pyrolysis*, vol. 135, 2018.

3. Lab-scale pyrolysis, and kinetic study of oil shale and kerogen

Oil shale pyrolysis can be used to simulate the hydrocarbon generation mechanism of source rocks in the subsurface[185]. The kerogen present in oil shale is bound with the mineral matter and decomposes simultaneously. The association of kerogen with the minerals may influence the diagenesis process[58]. There is significant interest and debate about prospective variance in kinetic parameters obtained from pyrolysis of parent oil shale and isolated kerogen[48, 186]. Another issue is whether the minerals catalyze kerogen decomposition to delay the vaporization temperature of hydrocarbons, leading to the occurrence of coking and cracking reactions. [186]. Therefore, a detailed study on the maturation pathway of kerogen and a thorough understanding of its synergy with inherent minerals is of significant importance.

This chapter presents a complete physicochemical and thermochemical analysis of Indian oil shale and extracted kerogen and provides a comprehensive kinetic analysis of their pyrolysis process. Nonisothermal pyrolysis kinetics of the Indian oil shale sample and extracted kerogen has been carried out using isoconversional methods. TGA-FTIR was used to study the thermal degradation of the oil shale and isolated kerogen, by simultaneous analysis of the evolved gases produced during the pyrolysis process. From the TGA data, lab-scale pyrolysis experimental matrix was setup using RSM optimization technique. The pyrolytic oil obtained at the optimum condition was subjected to characterization using GC-MS and NMR spectroscopy. The isolated kerogen was pyrolysed in a lab-scale pyrolysis setup, and the obtained oil was compared with the oil produced from pyrolysis of oil shale sample and solvent extracted bitumen using ^1H NMR analysis to study the catalytic effect of minerals leading to coking of produced hydrocarbons. The entire pyrolysis mechanism of kerogen and oil shale was studied under an inverted microscope to visualize the degradation mechanism predicted by kinetic study.

3.1. Physicochemical characterization of oil shale

The ultimate and proximate analyses showed that oil shale sample obtained from Upper Assam, India contains 30.06% carbon, high sulfur content of 3.61%, 31.78% volatile matter and ash content of 53.93%. The high sulfur percentage shows the oil shale to be sour in nature. The percentage of carbon in Indian oil shale was found similar to Huadian & Gonglangtuo oil shales of China [34, 187] and Kukersite oil shale of Estonia [15], and was found to be higher than most oil shales around the world such as Green River, Colorado, Israeli, Australian and Jordanian oil shales [13, 16, 28, 188]. A comparison of Upper Assam oil shale with oil shales from different places around the world is summarized in Table 3.1.

The characterization of the inherent organic matter (kerogen) in the oil shale sample was studied by Rock-Eval analysis. Rock-Eval analysis of the Indian oil shale sample showed hydrogen index (HI) and oxygen index (OI) of 217 (mg/g), and 5 (mg/g), respectively. Plotting the values of HI and OI on the Van-Krevelen diagram[152] showed the kerogen to be of type II. The total organic carbon (TOC) was calculated in both dry and wet basis and was recorded to be 6.11% and 18.32%, respectively. The comparison of Rock-Eval analysis of Indian oil shale with different samples worldwide is tabulated in Table 3.2.

FTIR analysis showed the presence of the alcohols, phenols, aliphatic, aromatic and sulfur stretching and bending overlapped with silica and clay mineral, such as quartz, kaolinite, illite, and feldspar (Fig 3.1 and Table 3.3). The intensity of silica impurities was observed to be much higher. Hydroxylic group bands were observed from 3300 cm^{-1} to 3500 cm^{-1} . A sharp peak corresponding to phenol and alcohol groups was observed at 3625 cm^{-1} . Presence of aliphatic compounds was seen from 2500 cm^{-1} to 3000 cm^{-1} with a sharp peak at 2925 cm^{-1} . The aromatic bending was observed from 680 cm^{-1} to 860 cm^{-1} , with two sharp peaks at 692 cm^{-1} and 791 cm^{-1} . The presence

of silica impurities was observed from 1100 cm^{-1} to 1020 cm^{-1} with a sharp peak at 1033 cm^{-1} depicting quartz.

The presence of minerals plays a significant role in the pyrolysis process. As reported in earlier works [24, 25] the presence of carbonate minerals restricts the emission of sulfur compounds and the silica compounds act as inhibitors to heat transfer during pyrolysis. XRD analysis (Fig. 3.2) showed the oil shale sample to contain abundance of silica compounds, and low percentage of calcite and dolomite (Table 3.4). Presence of pyrite was also detected which indicates the presence of inorganic sulfur. Higher percentage of silica compounds (92.30%) manifests that the Upper Assam oil shale can be classified as silicious type. As the oil shale has low amount of carbonate minerals (1.30% calcite and 1.10% dolomite), it may promote emission of sulfur compounds during pyrolysis. The effect of higher percentage of silica can be observed in the higher activation energy as perceived from the kinetic study of the oil shale pyrolysis process (Section 3.5).

Table 3.1. Characteristics of Upper Assam oil shale and comparison with different oil shales around the world.

Oil Shales	C (wt%)	H (wt%)	N (wt%)	S (wt%)	Moisture (wt%)	Ash (wt%)	Volatile Matter (wt%)	Fixed Carbon (wt%)	TOC (wt%)
Upper Assam ^(a)	30.06	2.80	1.44	3.61	4.43	53.93	31.78	9.86	6.11-18.2
Kukersite[15, 114]	27.90	2.90	0.02	0.86(avg)	1.30	47.88	46.25	4.57	36.40
Green Rive[13, 71, 189]	17.45	1.60	0.53	0.18	0.30	66.80	33.20	0.00	15.80
Colorado[139, 188, 189]	17.50	2.50	0.50	0.60	1.9	61.90	26.90	11.20	10.66
Huadian[14, 125]	29.23	4.28	0.61	4.92	3.26	56.91	39.34	3.75	8.70(avg)

^(a) = Tikak Colliary, Makum Coal Field, India

*Oxygen content have been calculated by difference ($O=100-(C+H+N+S)$)

Table 3.2. Rock-Eval analysis of Indian oil shale and comparison with different oil shale samples around the world.

Sample	Hydrogen Index (mg/g)	Oxygen index (mg/g)	T _{max} (°C)	Kerogen type
Indian oil shale (Present study)	217	5	427	Type II
Kukersite oil shale[190]	1005	13	----	Type I
Green river oil shale[191]	862.31	5.38	438.1	Type I
Huadian oil shale[192]	766	12	438	Type I
Gippsland oil shale[193]	245	----	432	Type II
Turkish oil shale[194]	513	45	432	Type II

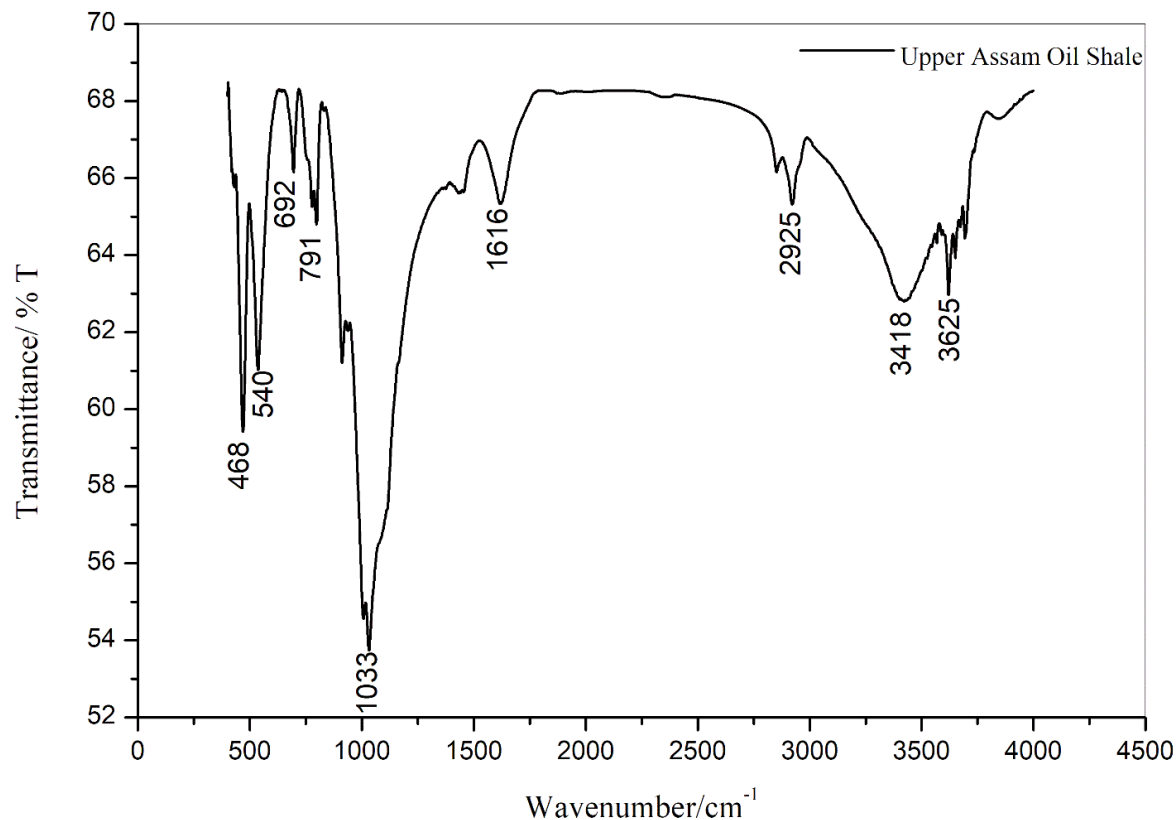


Fig 3.1. FTIR spectra of Upper Assam oil shale sample.

Table 3.3. Different functional groups detected by FTIR analysis of the Upper Assam oil shale.

Wavenumbers (cm ⁻¹)	Functional Groups
3625	-OH group; Alcohols and Phenols (strong; sharp)
3300-3500	-OH stretch from -COOH and -COH
3000-2500	C-H stretch; Alkanes; Carboxylic Acid Stretch
1600-1650	Aromatic -C=O vibration; -C=O stretch from H-bonded conjugate
1020-1100	Silicate Impurities; quartz
860-680	Aromatic C-H Stretch;
680-610	S-O bending; sulphates

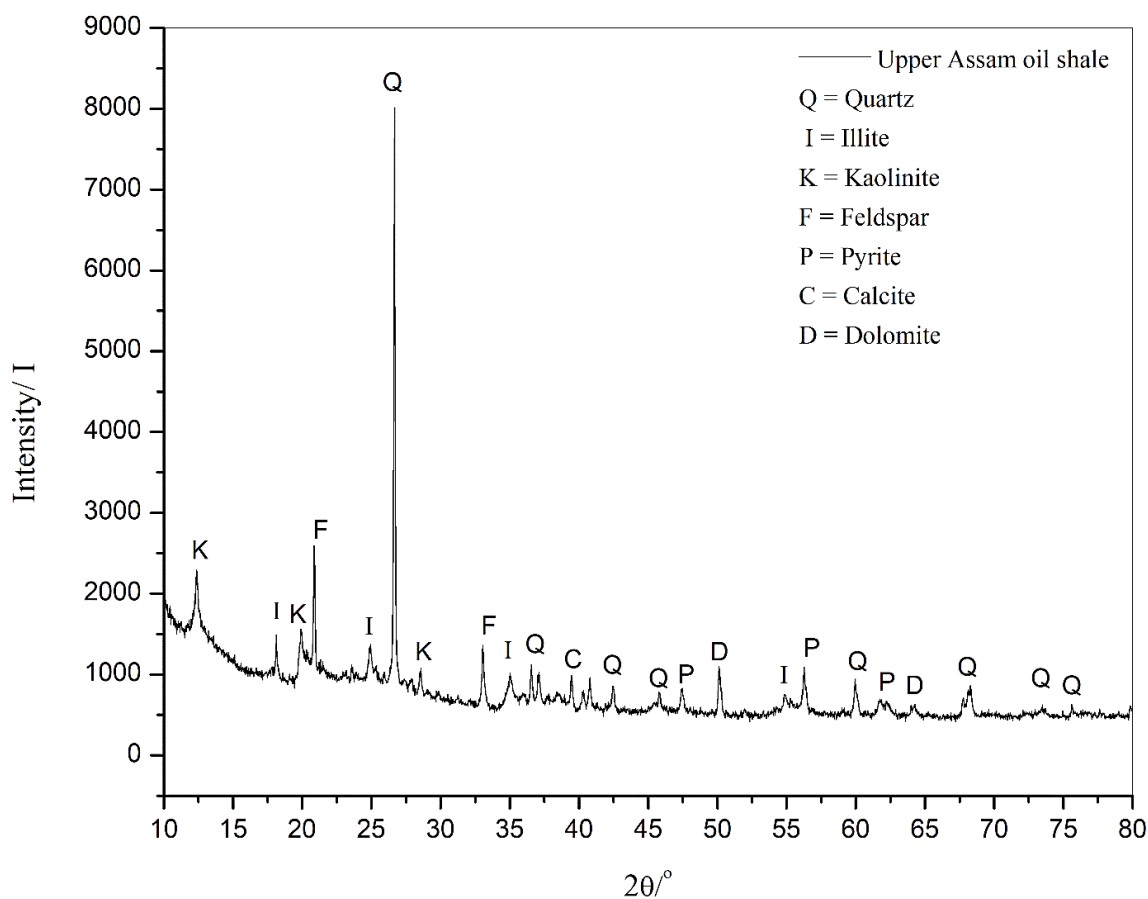


Fig 3.2. XRD spectra of Upper Assam oil shale.

Table 3.4. XRD spectra analysis of oil shale.

Minerals	Formula	Type	Percentage (%)
Quartz	SiO ₂	Silicious	46.30
Illite	(K,H ₃ O)(Al,Mg,Fe) ₂ (Si,Al) ₄ O ₁₀ [(OH ₂),H ₂ O]	Silicious (Clay)	21.30
Kaolinite	Al ₂ O ₅ Si ₂ (OH) ₄	Silicious	15.40
Feldspar	Al ₂ O ₈ Si ₂ Sr	Silicious	9.30
Pyrite	FeS ₂	Sulfur	5.20
Calcite	CaCO ₃	Carbonate	1.30
Dolomite	C ₂ CaMgO ₆	Carbonate	1.10

3.2. Extraction of kerogen

Acid solvent demineralization has been proved as an effective process for removing inorganic matter from oil shale[61, 62]. The results of different steps of demineralization of oil shale are summarized in Table 3.5 along with standard deviation. TG analysis of the oil shale sample showed 81.71% of mineral matter present in it. Solvent extraction with CH₃OH and DCM led to extraction of 7.30 wt% of bitumen from the initial weight of the oil shale sample. And, leaching with 10% concentration HCl removed a total of 4.64 wt% carbonate minerals. Further, 3.4 wt% pyrite was removed by 20% concentration HNO₃. Around 84 wt% silica minerals were removed by leaching with HF at room temperature. The demineralization process resulted in the removal of 97.78 wt% from the total mineral matter content from the total mass of the oil shale sample. For the identification of the sample after each stage of demineralization, the oil shale sample is designated as OS-1. The bitumen free oil shale is named as OS-2, carbonate and bitumen free oil shale is named as OS-3, pyrite, carbonate, and bitumen free oil shale are named as OS-4, and the oil shale free of silica, pyrite, calcite, and bitumen (extracted kerogen) is termed as OS-5.

3.3. Physicochemical characterization of extracted kerogen

The comparison of physicochemical properties of extracted kerogen with Indian oil shale and other kerogens from around the world is shown in Table 3.6. Kerogen showed 75 wt% of carbon, 8 wt% hydrogen, 2.06 wt% of sulfur, 1 wt% nitrogen, 13.99 wt% oxygen, 1.30 wt% moisture, 2.08 wt% ash, 92.05 wt% volatile matter, and 4.57 wt% fixed carbon. Kerogen exhibited total organic carbon content of 71.40 wt%. The decrease in the percentage of sulfur in extracted kerogen has occurred due to the removal of pyrite from the oil shale sample. The kerogen was identified to be type II based on the Rock-Eval analysis of the parent oil shale sample (section 3.1).

Table 3.5. Steps for demineralization of oil shale.

Mineral/Compound	Solvent/Acid used	Initial weight (g)	Final weight (g)	Weight loss (g)	Standard deviation
Bitumen	1:4 MeOH & DCM	50	46.30	3.70	0.84
Carbonate	10% conc. HCl	46.30	44.15	2.15	1.07
Bitumen	1:4 MeOH & DCM	44.15	44.01	0.65	0.40
Pyrite	5% conc. HNO ₃	44.01	42.95	1.06	0.59
Bitumen	1:4 MeOH & DCM	42.95	42.95	0.003	0.00
Silica compounds	Conc. HF	42.95	6.58	36.37	2.54

Total percentage of bitumen and minerals removed = $[(3.7+2.15+0.65+1.06+0.003+36.37)/50] \times 100 = 87.78 \text{ wt/wt}\%$

Table 3.6. Characteristics of Indian origin kerogen and oil shale and compared with kerogen samples from different origins.

Sample	Ultimate analysis					Proximate analysis				TOC (wt%)	H/C ratio
	C (wt%)	H (wt%)	N (wt%)	S (wt%)	O (wt%)	Moisture (wt%)	Ash (wt%)	Volatile Matter (wt%)	Fixed Carbon (wt%)		
Indian kerogen (present study)	75	8	1.00	2.06	13.99 ^a	1.30	2.08	92.05	4.57	71.49	1.12
Kukersite kerogen[195]	65.74	7.39	0.37	3.34	23.16	1.5	37.4	----	----	39.67	1.35
Sot basin, Northern Thailand[195]	69.11	9.28	1.88	2.48	17.25	3.4	53.6	----	----	29.53	1.61
North Sea kerogen[195]	56.42	7.75	1.93	31.49	2.41	6.3	83.4	----	----	7.38	1.65
Green river kerogen[196, 197]	77.4	9.8	2.8	2	8	----	5.20	----	----	----	1.54
Huadian kerogen[61]	77.52	10.54	1.72	2.14	-----	----	2.62	----	----	77.39	1.63
Kimmeridge Blackstone kerogen[198]	62.52	6.49	1.70	11.31	5.58	----	----	----	----	62.52	1.24

^a = Oxygen content have been calculated by difference ($O=100-(C+H+N+S)$)

XRD analysis was performed after each step of the demineralization process (Fig 3.3) to verify the removal of desired minerals from the oil shale sample. The quantification of minerals present in the raw oil shale and the oil shale sample after each step of demineralization till pure kerogen was obtained is presented in Table 3.7. XRD analysis of the oil shale sample showed it to be siliceous (92.30% silica compounds, 2.4% calcite compounds)[151]. The spectra of kerogen showed the absence of any minerals previously present in the oil shale sample, with a trace amount of illite (1.2%) and kaolinite (0.8%). These may have occurred due to the presence of residue clay minerals on the surface of kerogen during washing. The residual silica minerals may be the reason for the occurrence of 2.2 wt% ash content observed during proximate analysis. A baseline shift was observed from $2\theta = 10^\circ$ to 30° , which agrees with the presence of organic matter[199].

FTIR spectra of the oil shale sample after removal of bitumen and each step of demineralization are shown in Fig 3.4. The identified functional groups and their relative concentrations at each step of demineralization is summarized in Table 3.8. FTIR analysis of kerogen showed the extracted kerogen to be free of mineral matter with the presence of alcohols, phenols, aliphatic, aromatic, and small percentage sulfur stretching corresponding to sulfates. The presence of aliphatic compounds was observed at $2500\text{--}3000\text{ cm}^{-1}$ with a sharp peak at 2925 cm^{-1} . The aromatic bending was observed from 680 to 860 cm^{-1} and 1400 to 1660 cm^{-1} with a sharp peak at 1616 cm^{-1} . A sharp peak corresponding to phenol and alcohol groups was observed at 3625 cm^{-1} . FTIR spectra for each step of demineralization showed no notable change in concentration of different functional groups present in the kerogen sample compared to the parent oil shale. The parent oil shale (OS-1) and demineralized kerogen sample (OS-5) showed an identical distribution of OH stretching (3300 cm^{-1}), CH aliphatic (2925 cm^{-1}), C-C aromatics (1616 cm^{-1}), and SO compounds (692 cm^{-1}). This showed that the kerogen was not chemically altered during the demineralization process.

FESEM-EDX analyses of oil shale and kerogen samples showed their surface morphology and elemental composition. Oil shale appeared to be a porous, heterogeneous mixture of carbon, oxygen, sulfur, and nitrogen coexisting simultaneously with mineral matter. The organic matter in oil shale is present in the inherent surface pores (Fig 3.5). EDX of oil shale showed 37.20% carbon, 46.3% oxygen, 2.8% sulfur, 2% nitrogen, 7.9% silicon, 1% calcium with trace amounts of aluminum (1%), iron (1.3%) and magnesium (0.1%). The morphology of kerogen appeared as an agglomerate of lumped structures, comprising purely of 78.90 % carbon, 18.20 % oxygen, and 2.90 % sulfur with the absence of any mineral matter. The presence of sulfur may signify the existence of organic sulfur in the kerogen. This further confirmed the absence of mineral matter in the extracted kerogen and, the kerogen samples can be subjected to thermochemical study for investigation of thermal maturation kinetics of kerogen. However, it may be noted that as FESEM-EDX analysis is a surface technique[200], therefore small variation is observed in the concentration of identified elements compared to CHNS and XRD analyses.

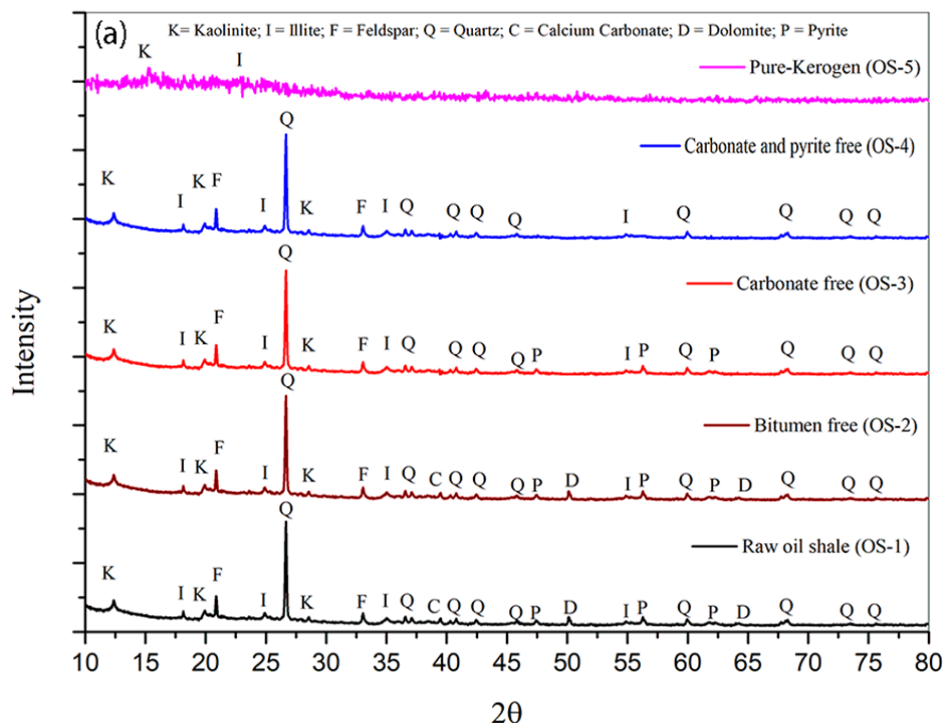


Fig 3.3. XRD spectra of oil shale and extracted kerogen samples. The sharp peaks in oil shale are due to the crystalline behavior of the predominant silica and other minerals.

Table 3.7. XRD spectra of the samples obtained from different steps of demineralization of oil shale.

Category	Minerals	OS-1 (oil shale) (%) [151]	OS-2 (%)	OS-3 (%)	OS-4 (%)	OS-5 (Kerogen) (%)
Siliceous	Quartz	46.30	46.61	46.40	48.40	0.2
	Illite	21.30	21.40	22.50	22.50	1.2
	Kaolinite	15.40	15.30	16.60	17.90	0.8
	Feldspar	9.30	9.21	9.30	9.30	0
Sulfur	Pyrite	5.20	5.19	5.20	0	0
Carbonate	Calcite	1.30	1.20	0	0	0
	Dolomite	1.10	1.10	0	0	0

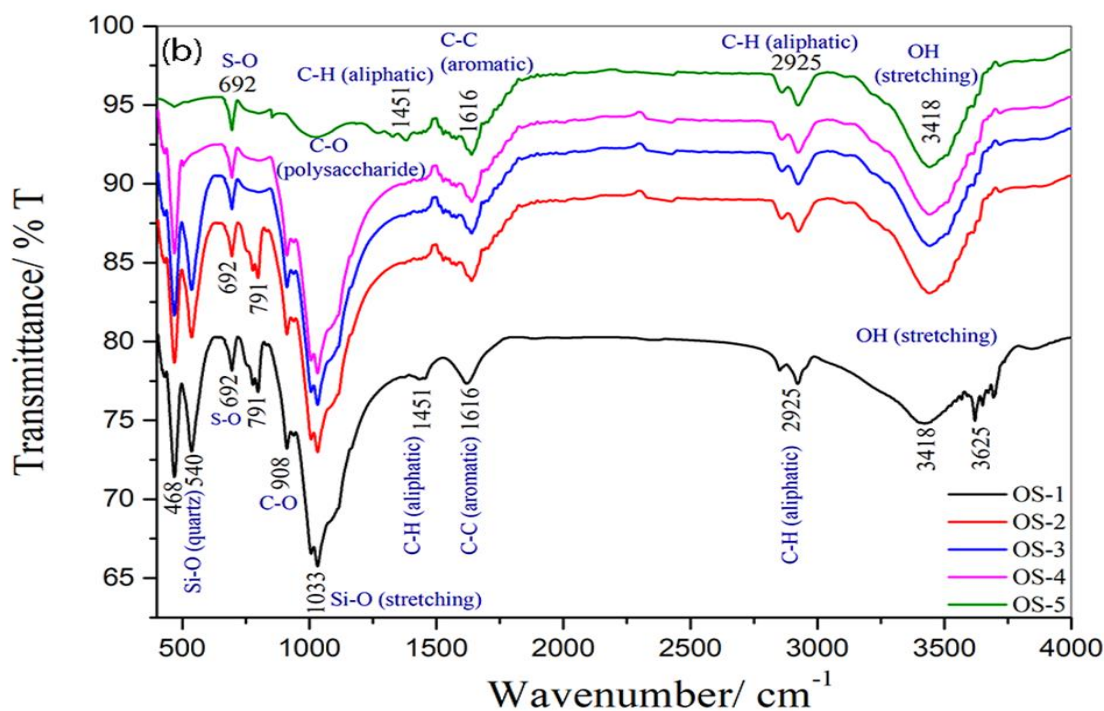


Fig 3.4. FTIR spectra of extracted kerogen and oil shale show the absence of silica minerals in the extracted kerogen.

Table 3.8. Relative area concentration of functional groups of FTIR spectra of the samples obtained from demineralization of oil shale.

Wavenumber (cm ⁻¹)	Functional Groups	OS-1 (%) (Oil shale)	OS-2 (%)	OS-3 (%)	OS-4 (%)	OS-5 (%) (Kerogen)
2925	CH (aliphatic)	6.60	6.05	7.01	8.21	15.94
3300	-OH	13.20	11.54	11.60	12.50	32.85
1150	C=O	6.52	5.75	5.60	5.01	8.95
1400-1660	Aromatics	5.59	4.72	4.80	5.87	14.50
1000-1200	Phenolic, ether and alcohol	8.04	6.90	6.94	7.61	25.70
680	SO compounds	5.57	5.50	5.45	1.98	2.01
1030	Si-O clay minerals	37.21	38.81	41.21	40.31	0
500-450	Quartz	13.71	16.90	17.31	18.50	0
710-867	Carbonate	3.62	3.74	0	0	0

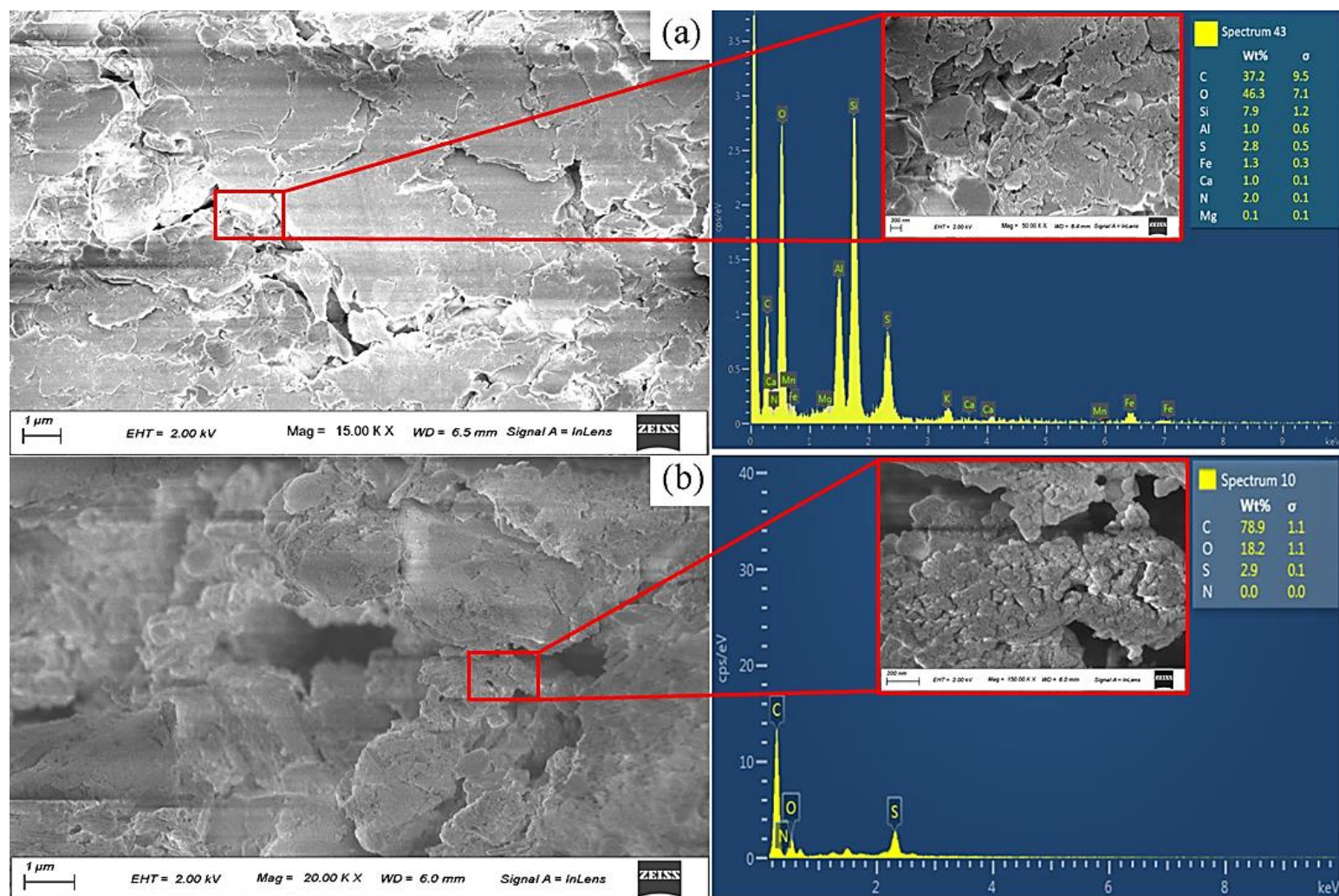


Fig 3.5. FESEM-EDX images of (a) oil shale and (b) kerogen samples. EDX analysis shows extracted kerogen to be free of mineral matter.

3.4. Thermogravimetric analysis and Differential thermogravimetry (TG-DTG)

Thermogravimetric analysis was used to analyze the thermal decomposition behavior during the pyrolysis process of the oil shale sample, and isolated kerogen. Four different heating rates were considered at 10, 20, 30 and 50 °C/min (Fig 3.6(a)). For the oil shale sample, the TG curves showed that a total 4 wt% moisture loss in the pre-heating zone occurs from 35 to 170°C. Significant decomposition corresponding to organic matter content (21 wt%) was observed from 300 to 700°C due to decomposition of the organic matter present in oil shale. Mineral matter decomposition has been reported to occur from 600 to 800°C primarily due to decomposition of carbonate minerals [24, 25]. From 700 to 1000°C a continuous mass loss was observed. However, in the present study, as seen in the TG-DTG plot, there was no notable occurrence of mineral matter decomposition, as the dominant minerals present in the oil shale sample were silica compounds, and the degradation of silica compounds occur above 1200 °C. Minute amount of carbonate minerals (2.4%) was detected by XRD analysis. The continuous slope in the range of 700 to 1000°C may have occurred because of decomposition of clay minerals (such as illite and kaolinite) and the minute amount of carbonate minerals. The onset temperature, maximum decomposition temperature, and offset temperature corresponding to the pre-heating and organic decomposition region for the oil shale sample at each heating rate is shown in Table 3.9. The thermal decomposition behavior of isolated kerogen was studied by TG analysis at four heating rates of 10, 20, 30, and 50 °C/min from 30°C to 800°C (Fig 3.6(b)). Identification of the pyrolytic zone with the onset, maximum decomposition, and offset temperatures is shown in Table 3.9. The valorization of kerogen starts around 200°C up to 600°C. The DTG curves showed the organic decomposition to occur as an overall single-stage decomposition. The organic degradation of oil shale did not initiate until 300°C. This is because of the mineral matrix envelope over the kerogen in the case of oil shale [13, 201].

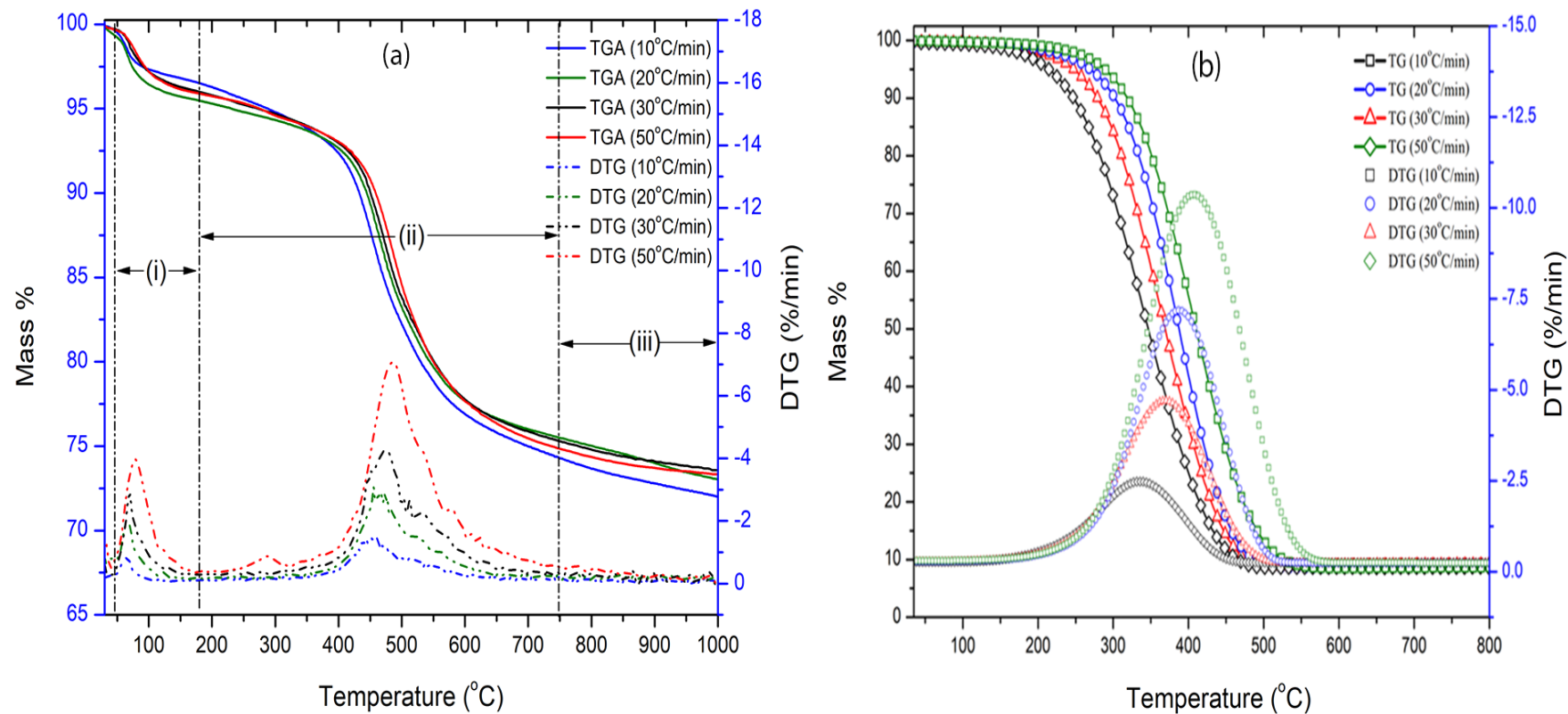


Fig 3.6. TG-DTG curves of (a) Upper Assam oil shale at different heating rates of 10, 20, 30 & 50 °C/min from 30 to 1000 °C & differentiating (i) moisture loss (ii) organic decomposition (iii) mineral matter decomposition, and (b) isolated kerogen at heating rates of 10, 20, 30 & 50 °C/min from 30 to 800 °C.

Table 3.9. Onset, offset and maximum decomposition temperature values of organic matter decomposition for oil shale and kerogen.

Heating rate(°C/min)	oil shale				kerogen			
	Onset Temperature (°C)	Maximum Decomposition (°C)	Offset Temperature (°C)	Mass loss (wt%)	Onset Temperature (°C)	Maximum Decomposition (°C)	Offset Temperature (°C)	Mass loss (wt%)
10	351.2	457.9	630.6	21	175.5	365.1	450.0	90.3
20	363.1	464.6	651.0	21	185.2	385.5	485.2	90.3
30	375.0	476.5	681.4	21	190.7	402.2	520.3	90.3
50	383.5	483.3	694.2	21	202.0	425.2	572.7	90.3

3.5. Kinetic study

3.5.1. Determination of apparent activation energy values

TG data at four heating rates of 10, 20, 30, and 50°C/min for the organic decomposition region of the oil shale sample, and kerogen isolated from the oil shale were used to estimate the kinetic parameters by using model free isoconversional methods (Section 2.13). The errors in the determined apparent activation energy values were estimated by triplicating the TG runs and calculating the apparent activation energy values for different heating rate combinations of 10, 20, 50 °C/min and 10, 20, 30, and 50°C/min.

For the oil shale sample, the organic decomposition region was considered for determination of the kinetic parameters. The organic matter decomposition zone was identified from the TG-DTG curve (Fig. 3.6(a)), by identifying the onset (300 °C) and the offset temperatures (700 °C), respectively. The activation energy was determined by both linear and non-linear differential and integral methods, viz. Friedman (differential), Starink, and Advanced Isoconversional (AIC) method (integral). Friedman method showed a mean apparent activation energy of 249.75 kJ/mol with a mean error of 4.5%, whereas Starink and AIC method showed mean apparent activation energy values of 241.20 kJ/mol & 239.68 kJ/mol with mean error percentage of 3.5%, and 2.7%, respectively. The apparent activation energy values obtained for the Upper Assam oil shale was observed to be similar to those reported for Huadian oil shale [202] Green River oil shale [27], Moroccan oil shale [45, 136], and Kukersite oil shale [203]. The distribution of the apparent activation energy values for the considered isoconversional methods are presented in Fig 3.7(a).

The decomposition region for kerogen was identified as (200°C to 600°C) was determined from the TG-DTG curves at four heating rates (10, 20, 30, and 50 °C/min) and considered for estimation of kinetic parameters (Fig 3.6 (b)). The apparent activation energies obtained from each method at

different heating rate combinations are presented in Fig 3.7 (b). The mean errors in the apparent activation energy values were found to be 4.1%, 3.5%, and 3% for Friedman, Starink and, AIC method respectively. The apparent activation energy values increased with increase in conversion for each isoconversional method. Friedman method showed a mean apparent activation energy value of 229 kJ/mol, while, Starink method showed a mean apparent activation energy value of 219 kJ/mol. AIC method showed a mean apparent activation energy value of 236 kJ/mol. The activation energy values obtained for Indian-origin oil shale and kerogen were in range with activation energy values of different kerogens from around the world (Table 3.10). The mean apparent activation energy values for the isolated kerogen sample were found to be similar to mean apparent activation energies of Indian oil shale (243.54 kJ/mol)[151] considering the error percentage. Similar results have been reported previously by Burnham and team[58, 204], and Pan et al.[59], who showed that decomposition of mineral matter has no significant influence on the apparent activation energy values of kerogen.

The increase in apparent activation energy values with increase in conversion for both oil shale and kerogen can be explained by the generation of different compounds during kerogen pyrolysis compared to oil shale as identified by TG-FTIR (Fig 3.13 (a-f)). The occurrence of lower activation energy values during the beginning of the reaction ($\alpha < 0.2$) is due to the cracking of weak chemical bonds in the kerogen leading to the generation of water molecules and light hydrocarbon compounds[60]. This can be observed by the initial occurrence of CH aliphatic compounds (Fig 3.13(a)), low intensity of aromatic compounds which may have occurred by the degradation of phenolic compounds (Fig 3.13(b)), along with –OH group compounds (Fig 3.13(d)), and CH₄ (Fig 3.13(c)). The gradual increase in activation energy from $0.2 < \alpha < 0.7$ could owe to the swelling and decomposition of kerogen into hydrocarbons. This is observed by the sharp rise in the intensity of

CH aliphatic compounds (Fig 3.13(a)), aromatics (Fig 3.13(b)), -OH compounds (Fig 3.13(d)), with the initiation of CO₂ (Fig 3.13(e)) and small intensity of S=O compounds (Fig 3.13(f)). Further increase of activation energy from $\alpha=0.7$ to 0.98 may relate to releasing gases and lighter hydrocarbons and decomposition of bitumen followed by coking reaction[201]. This mechanism can be seen to occur due to the occurrence of aromatic compounds corresponding to $\alpha = 0.7$ to 0.98 with sharp increment at $\alpha = 0.8$ (Fig 3.13 (b)) and continuous evolution of CH₄ from $\alpha = 0.4$ to 0.9 and subsequently decrease from 0.9 to 0.98.

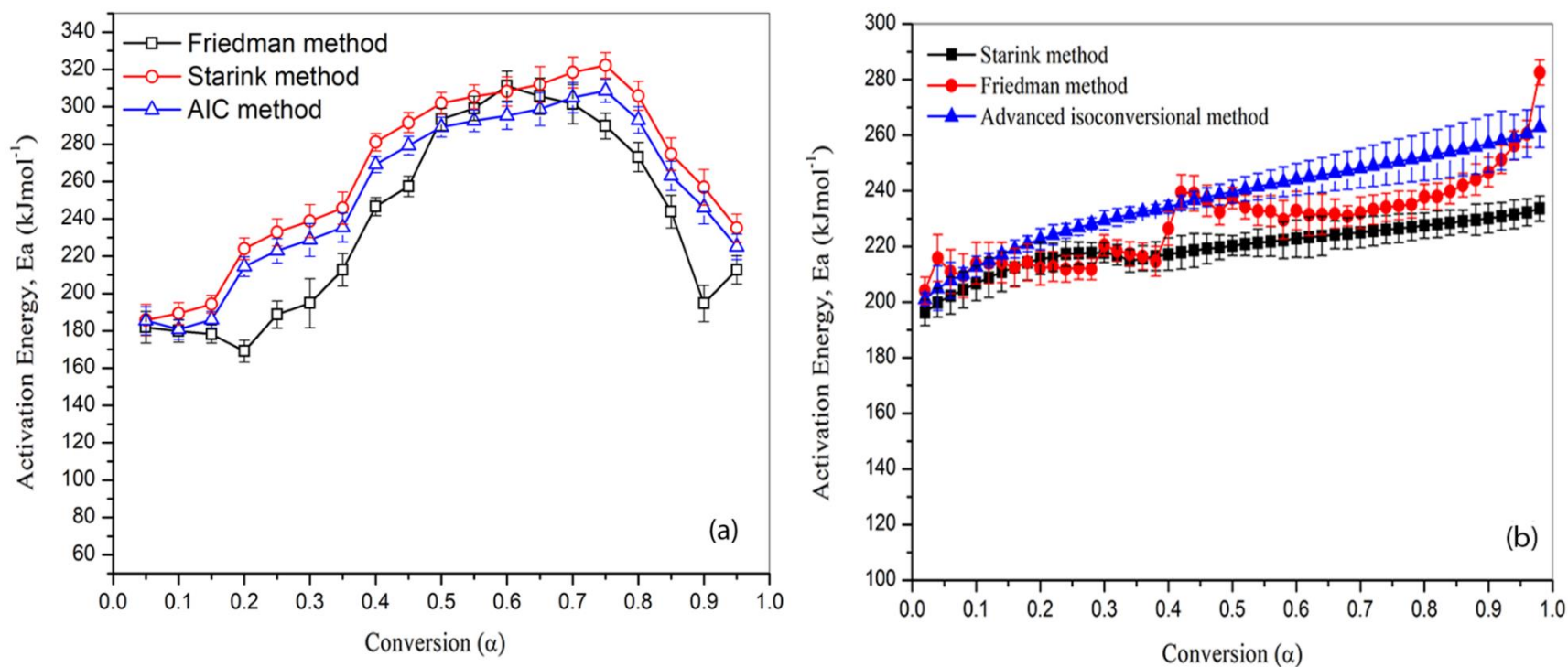


Fig 3.7. Distribution of apparent activation energy value for kerogen decomposition profile at heating rate combination of 10, 20, 30, and 50°C/min (a) for oil shale sample, and (b) extracted kerogen.

3.5.2. Determination of reaction model

The experimentally determined apparent activation energy was used for identification of the reaction mechanism by using the differential-integral $\left(\frac{Z(\alpha)}{Z(0.5)}\right)$ Criado master plot [180]. For determining the reaction mechanism or kinetic model the activation energy at $\alpha=0.5$ for each method has been considered. The experimentally determined master plots obtained at each heating rate were plotted against the standard theoretical master plots of different reaction mechanisms (section 2.13). The resultant plot shows the decomposition of oil shale to follow D-3 Diffusion mechanism till $\alpha = 0.8$ and fall upon A-2 Avrami Eroffev mechanism at $\alpha = 0.9$. Previous works on oil shale kinetics have shown the event of multiple reactions during oil shale pyrolysis [27, 42]. These multiple reactions may suggest the occurrence of heat diffusion, mass diffusion, nucleation growth and other subsequent reactions. The manifestation of the D-3 diffusion mechanism might occurred because of the diffusion of heat and mass through the pores of oil shale. The heat diffusion may occur due to the conductive heat transfer from the reactor to oil shale and from the mineral matrix to the kerogen mass and from the converted kerogen to the unconverted kerogen by both conductive and convective modes of heat transfer. The mass transfer corresponds to the diffusion of the liquid and gaseous products through the pores of oil shale after conversion of the kerogen and bitumen. The A-2 Avrami Eroffev, model observed at $\alpha = 0.9$ may justify the coking of the produced hydrocarbon products by the occurrence of secondary coking reactions predicted to occur during oil shale pyrolysis. AIC method showed higher co-relation factor for the experimental $f(\alpha)$ vs theoretical $f(\alpha)$ ($R^2=0.991$). Criado master plot using the values of activation energy obtained by the AIC method is shown in Fig. 3.8 (a). The Criado master plots for Friedman method and Starink method are shown in Appendix Fig A1 and A2, respectively.

The Criado master for degradation of isolated kerogen showed the occurrence of multiple reaction models such as F1, D3, A2, and A3 reaction models. However, F1 (first-order) and A2 (Avrami Eroffev nucleation) reaction models showed higher values of R^2 correlation. The Criado master plot for experimentally determined reaction models using AIC method is shown in Fig 3.10(c), and the Criado master plots for Friedman and Starink methods for kerogen pyrolysis are shown in Appendix Fig A3 and A4, respectively. The occurrence of each identified reaction model was found to be consistent for each heating rate on the conversion scale. The occurrence of the F1 reaction model may refer to the initial breakdown and release of lighter hydrocarbons. The formation of lighter hydrocarbons is due to the cracking of aliphatics into smaller alkanes[205]. Further decomposition processes, secondary and coking reactions may be conferred by the occurrence of the A2 Avrami Eroffev model [206]. Oil shale pyrolysis showed the event of the D3 Diffusion model followed by the A2 Avrami Eroffev reaction model in the presence of mineral matter[151]. The occurrence of the D3 Diffusion model may indicate the release of hydrocarbons from the pores on the surface of oil shale[72]. And, the occurrence of the A2 Avrami Eroffev reaction model may describe the catalytic effect of inherent minerals on the coking reaction of produced hydrocarbon vapors[186, 205]. Therefore, the kinetic study of kerogen can be summarized as the breakdown of heterogeneous macromolecules to release low molecular weight volatiles in the form of gaseous matter and the formation of char intermediates due to secondary cracking[157]. This shows that during oil shale pyrolysis, the kerogen degrades inside the mineral matrix into oil and gas before the produced products react with the mineral matter envelope as contemplated in oil shale pyrolysis.

3.5.3. Determination of pre-exponential factor

The compensation factor method was applied to the reaction models obtained from Criado master plot for both oil shale and isolated kerogen pyrolysis. For oil shale pyrolysis, the reaction order showed a high regression coefficient for D3 and A2 Avrami Eroffev model at different levels of conversion. These compensation parameters were used to evaluate the pre-exponential factor, A , at different conversions. The average value obtained is $2.56 \times 10^{19} \text{ sec}^{-1}$ for AIC method. The experimental $f(\alpha)$ values for each method were determined using E and A values and compared with the theoretical $f(\alpha)$ values. The comparison for values obtained for AIC model are shown in (Fig. 8 (b)). The variations in kinetic parameters with progress of decomposition uphold the multi model process; two reaction models D3 model up to $\alpha = 0.8$ and then shifts to A2 Avrami Eroffev model at $\alpha = 0.9$.

For kerogen pyrolysis process, the average values of the pre-exponential factor, A , at different conversions by compensation factor method are obtained as $2.41 \times 10^{19} \text{ sec}^{-1}$, $4.30 \times 10^{19} \text{ sec}^{-1}$, and $3.41 \times 10^{19} \text{ sec}^{-1}$ for AIC, Starink, and Friedman method, respectively. The variations in kinetic parameters with the progress of decomposition uphold the multi-reactions process. The experimental $f(\alpha)$ values were determined for each method using Ea and A values and compared with theoretical $f(\alpha)$ values of the reaction models identified from the Criado master plot. The experimental $f(\alpha)$ vs theoretical $f(\alpha)$ for AIC model is shown in Fig 3.8 (d). The linear correlation between $\ln(A)$ and apparent activation energy values (Ea) obtained by each isoconversional method for the identified reaction models are shown for AIC method to exhibit the highest mean R^2 value of 0.98, compared to 0.96, and 0.97 by Friedman, and Starink method respectively. This verifies the occurrence of multiple kinetic model compensation effects.

3.5.4. Reconstruction of thermogravimetric curves

The reconstruction of conversion plots from kinetic data showed the validation of similarity between the experimental profiles and the simulated profiles at different temperature programs.

For oil shale pyrolysis, the regression analysis for linearity fitting was performed for each heating rate (10, 20, 30 and 50 °C/min). AIC method showed highest average R^2 value of 0.992. Starink showed an average R^2 of 0.986, and Friedman method showed the lowest average R^2 value of 0.978. The simulated vs experimental profiles for AIC method for each heating rate are shown in Fig 3.9 (a-d). The simulated and experimental data profiles for Friedman, Starink, and AIC method with respect to experimental data obtained for oil shale pyrolysis at heating rate of 10°Cmin⁻¹ is shown in Fig 3.10(a). and the average linearity fitting co-efficient (R^2) corresponding to each method is shown in Fig. 3.10(b).

For kerogen pyrolysis, AIC method appeared to possess the highest average R^2 value (0.99) followed by Starink (0.985), and Friedman (0.97) methods. The experimental vs simulated profiles for AIC method for four heating rates are presented in Fig 3.11(a). Similarly, the reconstruction profiles for Starink and Friedman method at a heating rate of 10°C/min are shown in Fig 3.11 (b). Linearity fitting for profiles corresponding to each heating rate was performed by regression analysis and the average linearity fitting co-efficient (R^2) corresponding to each method is reported in Fig 3.11 (b). Based on the linear fitting and the R^2 average value AIC method is hereby considered to be the most appropriate method for determination of the apparent activation energy values for the pyrolysis process of the Indian oil shale and its isolated kerogen.

Comparison of the kinetic triplets obtained for the oil shale sample and isolated kerogen with oil shale and kerogen samples from other origins around the world is summarized in Table 3.10.

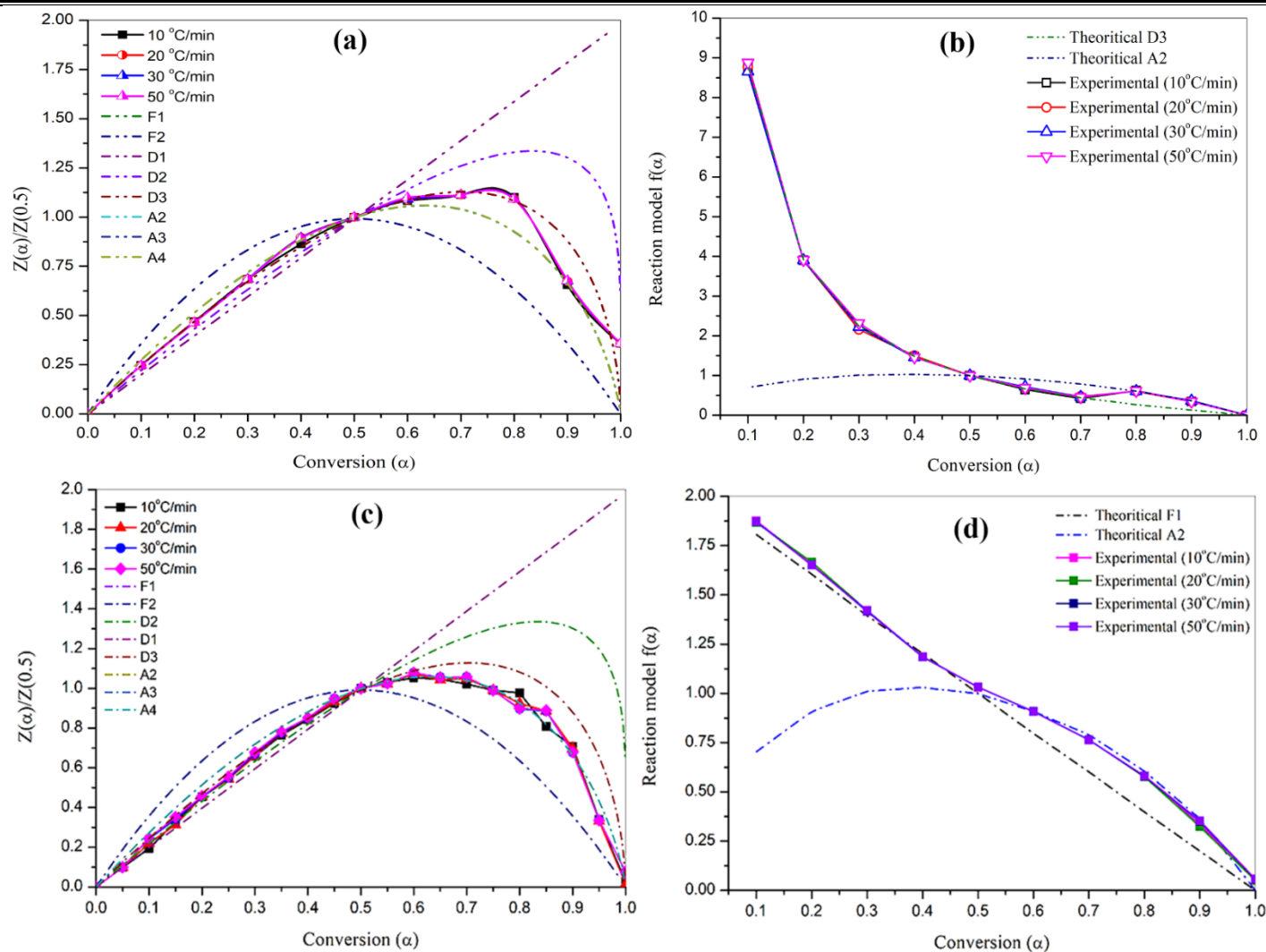


Fig 3.8. Experimental Criado master plots and reaction model, and Experimental $f(\alpha)$ vs theoretical $f(\alpha)$ for AIC method at each heating rate, for (a) and (b) oil shale, (c), and (d) isolated kerogen.

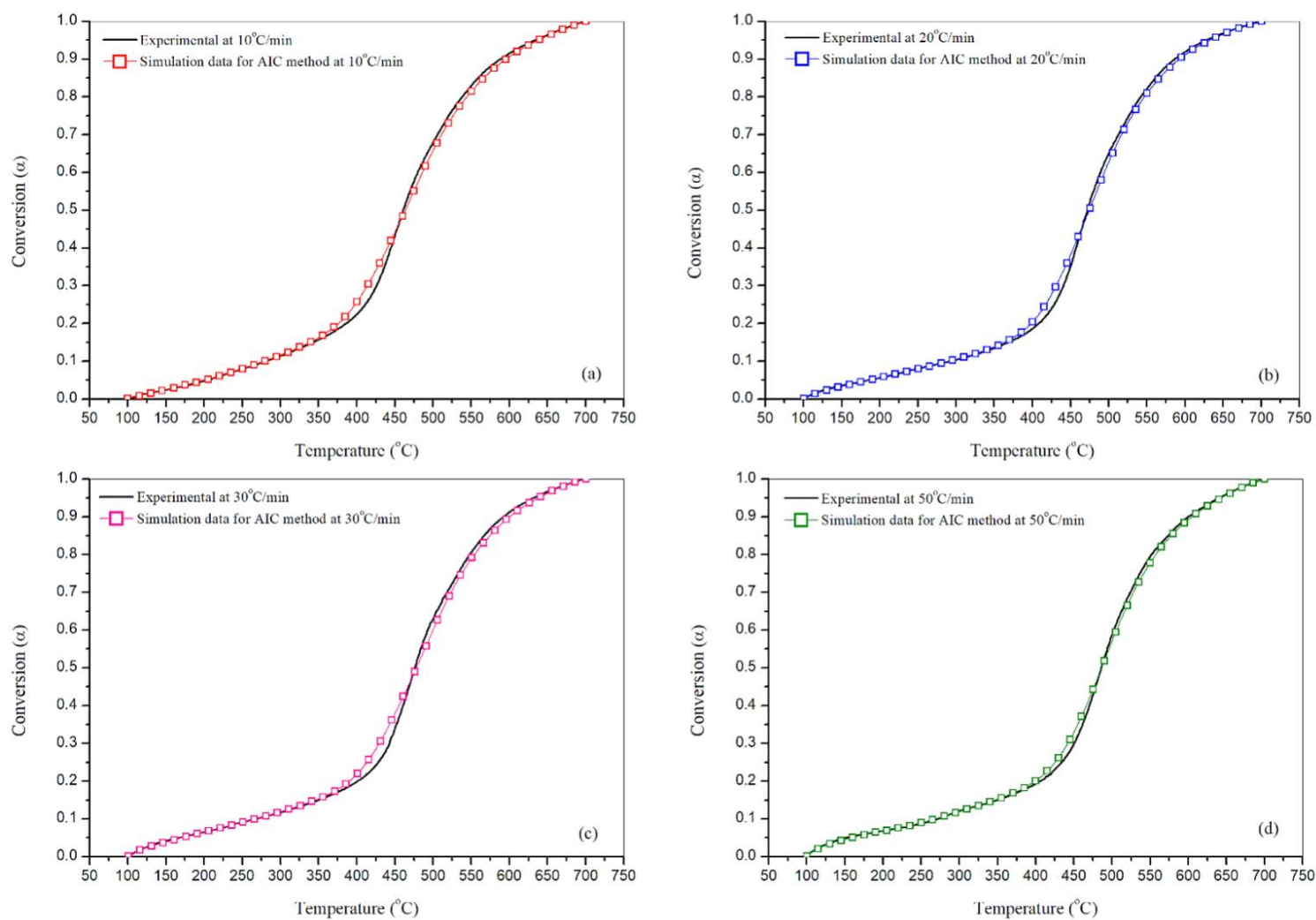


Fig 3.9. Fitness of experimental to simulated profile for AIC method at heating rate of (a) 10°C/min, (b) 20°C/min, (c) 30°C/min (d) 50°C/min.

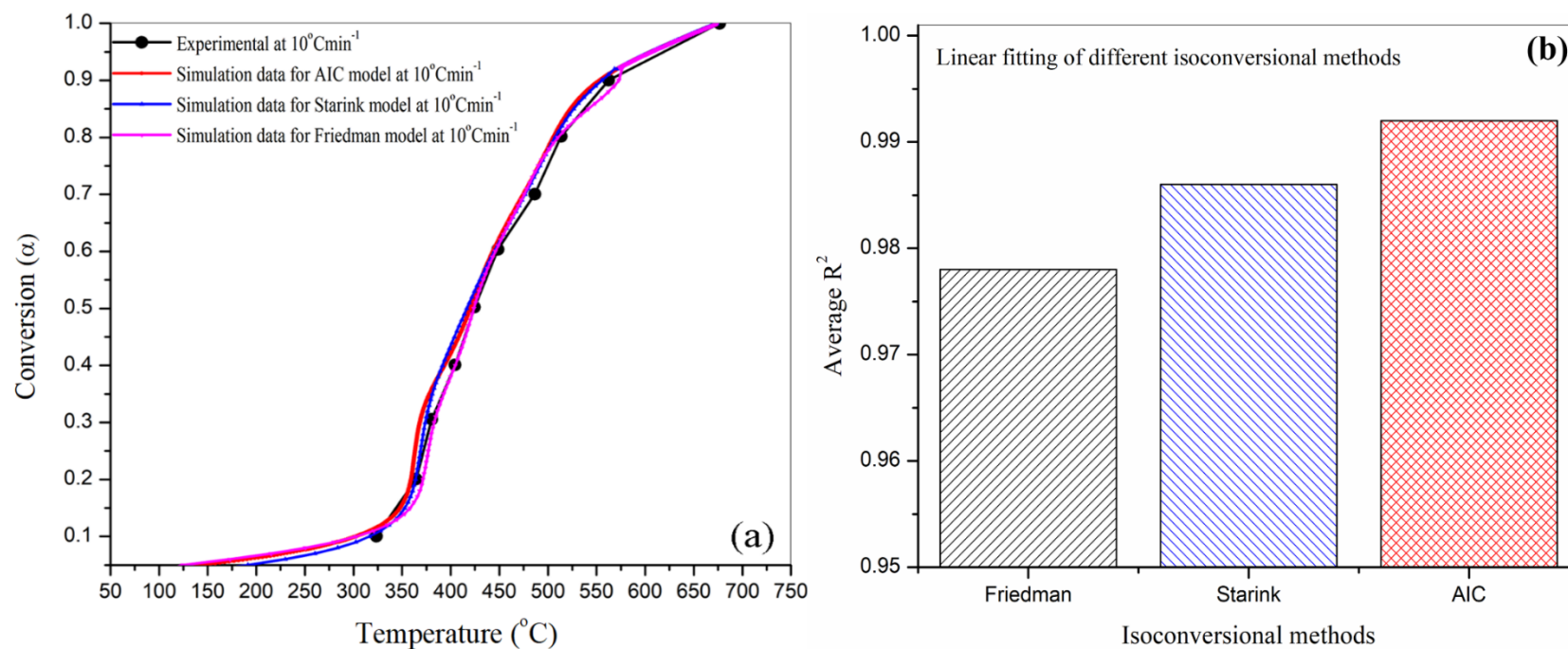


Fig 3.10. (a) Fitness of experimental to simulated profile for AIC, Friedman and Starink method at $10^{\circ}\text{C}/\text{mi}$, and (b) linear fitting of different isoconversional methods viz. AIC, Friedman and Starink method.

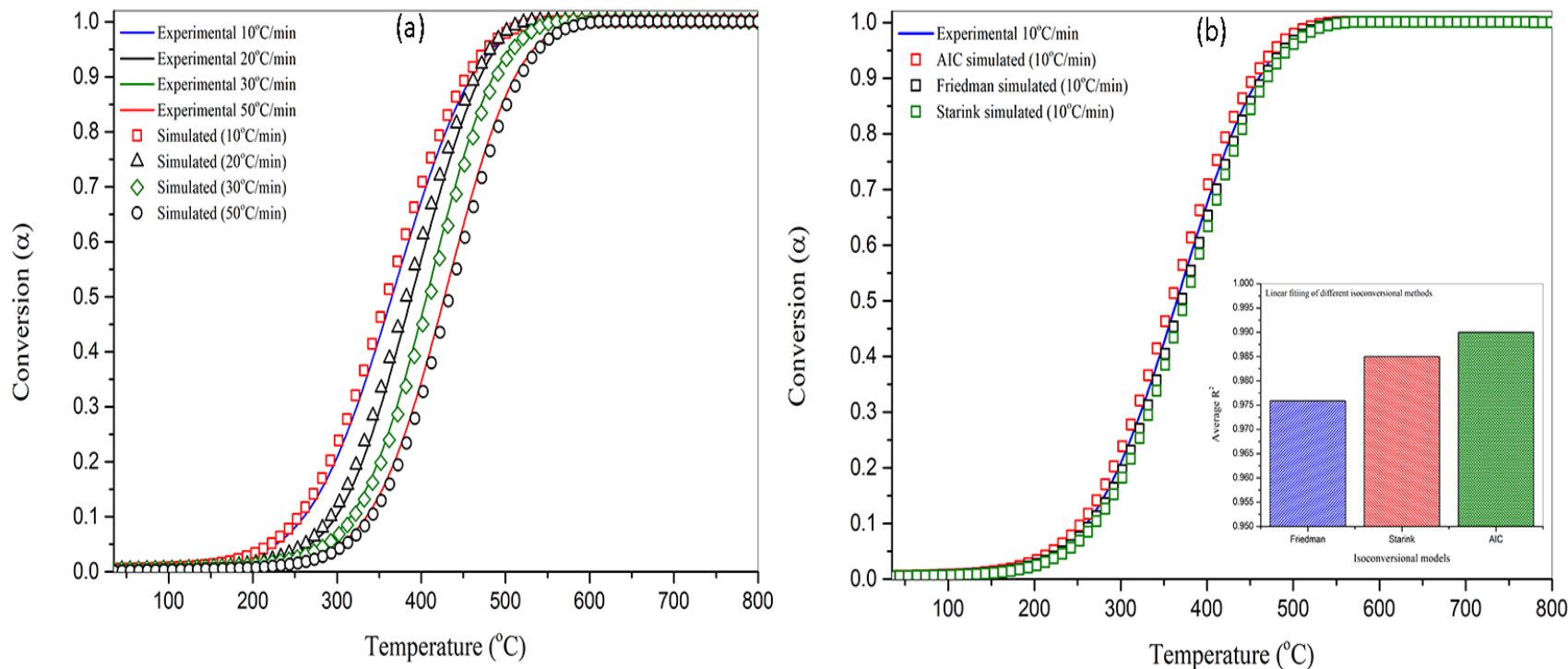


Fig 3.11. Experimental vs simulation plots for α vs T of kerogen pyrolysis (a) using AIC method (b) at 10 $^{\circ}\text{C}/\text{min}$ for Friedman, Starink, and AIC method. AIC method showed the highest linear average coefficient (R^2) of 0.99 between experimental and simulation profiles.

Table 3.10. Comparison of kinetic triplet values of different kerogen around the world.

Sample	Methodology for kinetic study	Mean activation energy values Ea (kJ/mol)	Mean pre-exponential factor A (sec ⁻¹)	Reaction models, f(α)
Indian oil shale (present study)	AIC method	247.5	2.56×10^{19}	D3 and A2
Indian Kerogen (present study)	AIC method	236	2.41×10^{19}	F1, and A2
Green river kerogen[201]	Isoconversional methods and DAEM	200	-----	F1 and F2
Kimmeridge clay kerogen[48]	DAEM	225	9.25×10^{15}	Parallel first order and nucleation model
Monterey shale kerogen[48]	DAEM	204	5.86×10^{15}	Parallel first order and nucleation model
Kimmeridgian black shale[57]	DAEM	210	$1.39 \times 10^{13} - 2.94 \times 10^{14}$	First order
Jimsar oil shale kerogen[59]	Isoconversional method	200	-----	-----
Australian torbanite kerogen[207]	Isoconversional method (Friedman method)	225	-----	n = 0.71 (less than first order)
Thailand kerogen[207]	Isoconversional method (Friedman method)	217	-----	n = 1.3 to 1.6 (near first order)
Indonesian kerogen[207]	Isoconversional method	230	-----	n = 3 to 4.4

	(Friedman method)			
Netherland kerogen[207]	Isoconversional method	230	-----	n = 3 to 4.4
	(Friedman method)			
Qatar kerogen[207]	Isoconversional method	220	-----	n = 1.9 to 2.4
	(Friedman method)			

3.6. Thermogravimetric analysis-Fourier transform infrared spectrometry (TG-FTIR)

Thermogravimetric analysis coupled with Fourier transform infrared spectroscopy (TG-FTIR) helps in visualizing the in-situ evolution of product vapors during pyrolysis or thermal degradation of oil shale and isolated kerogen. TG-FTIR plots of the evolved compounds for oil shale and kerogen at 20 °C/min are shown in Fig 3.12 (a) and (b), respectively. The recorded spectra for oil shale and kerogen showed the presence of C-H (stretching), C=C (aromatic bending), O-H (stretching), SO₂, and CO₂ occurring in the temperature range of 200°C to 600°C.

The FTIR spectra recorded the evolved gases during pyrolysis of oil shale and kerogen using the TGA-FTIR analysis. The recorded spectra shows the presence of C-H (stretching), CO₂, C=C (aromatic bending), O-H (stretching) and SO₂. Two large peaks were observed at 2250 cm⁻¹ – 2350 cm⁻¹ and 2850 cm⁻¹ – 3100 cm⁻¹, denoting CO₂ and C-H (stretching) respectively. The peak for CO₂ was generated between 350 to 550 °C. The generation of CO₂ occurred due to the reforming and cracking of the carbonyl and carboxyl group [61, 108]. C-H (stretching) peak was observed from 250 °C to 650 °C. The C-H (stretching) represented the aliphatic compounds formed during retorting with a small amount of aromatic compounds. The minute concentration of methane corresponding to wavenumber 3018 cm⁻¹ was observed from 250 °C to 650 °C with a sharp increment from 400 °C to 550 °C. The band occurring from 650 cm⁻¹ to 750 cm⁻¹ represents the C=C (aromatic bending). It stretched from 325 °C to 625 °C with two peaks occurring from 325 °C to 450 °C and 450 to 600 °C. O-H bond vibration was seen from 3500 cm⁻¹ to 4000 cm⁻¹. This represents the release of water, H₂O during retorting and starts from 175 °C and shows a sharp increment at 300 °C up to 475 °C. The generation of S=O compounds was observed between 1350 cm⁻¹ to 1400 cm⁻¹ and SO₂ was noted at 1374 cm⁻¹. S=O compounds were seen to occur from 275 °C, with a sharp peak at 375 °C, which decreased at 475 °C and later increased at 500 °C

finally ending at 650 °C. All the identified bands showed a sharp increment around 300 °C to 650 °C, which is the window of organic decomposition.

In kerogen, the primary product was C-H (stretching). The occurrence of the C-H (aliphatic) bond ranged from 250°C to 525°C in kerogen, as compared to 300°C - 600°C for oil shale [22]. This shows that the presence of mineral matter in oil shale hindered the organic decomposition, leading to an increase in the temperature range of evolved C-H group. A similar observation has been reported by Yan et al. [61] for the decomposition of Huadian oil shale and its kerogen. The higher apparent activation energy values obtained for oil shale compared to kerogen also support this observation. The comparison of the occurrence of compounds corresponding to different functional groups at different temperatures during pyrolysis of oil shale and kerogen is presented in Fig 3.13 (a-f). A broad spectrum occurred from 2100 cm⁻¹ to 2600 cm⁻¹ corresponding to –C=C– (Alkynes) in the temperature range of 250°C to 550°C, with a sharp increment at 400°C (Fig 3 (a)). A sharp peak of aromatic C-H (stretching) and C-H rock occurred in the range of 615 cm⁻¹ to 770 cm⁻¹, initiated at 250°C, and stretched up to 550°C (Fig3 (b)). The band of aromatics in oil shale pyrolysis appeared in a similar temperature range from 300°C to 600°C. A broad peak corresponding to methane (CH₄) (3018 cm⁻¹) appeared from 200 °C to 450 °C (Fig 3 (c)). Oil shale pyrolysis showed higher intensity of CH₄ to occur from 250°C to 500°C, and again from 550°C to 650°C. The high intensity of CH₄ observed during pyrolysis of oil shale may have occurred due to retrograde crosslinking reactions of aromatics leading to the generation of methane, hydrogen, and semi coke[205]. A broad spectrum corresponding to the O-H group occurred at 3502 cm⁻¹ to 3792 cm⁻¹ (300 to 500°C) and a low-intensity peak from 500°C to 650°C corresponding to the phenolic and alcoholic groups present in the kerogen (Fig 3 (d)). The release of C=C, C-H, and C=O functional group compounds was found much significant in kerogen than in oil shale as later

contains carboxylic acid salts comprising alkaline earth metals[61]. A trace amount of CO₂ was detected from 350°C to 450°C. However, for oil shale, the occurrence of CO₂ ranged from 350°C to 550°C[22]. The generation of CO₂ from the kerogen sample may have occurred due to the breakdown of carbonyl and carboxyl compounds[108], as the kerogen was free of carbonate minerals (Fig 3 (e)). A weak intensity of SO₂ and S=O compounds occurred from 250°C to 350°C and 400°C to 500°C due to the breakdown of organic sulfur bonds during emission of volatile compounds (Fig 3(f)). It was observed that for oil shale the band of SO₂ and S=O compounds ranged from 150°C to 600°C, owing to the decomposition of the inherent pyrite minerals in the oil shale sample along with decomposition of the organic sulfur bonds[22, 108]. TG-FTIR analysis showed that the volatilization temperature of C-H (aliphatic), CH₄, CO₂, and SO₂ were higher during pyrolysis of oil shale in the presence of minerals as compared to isolated kerogen pyrolysis. However, the spectra of C-H (aromatics) and OH (stretch) for oil shale pyrolysis did not show much variation from isolated kerogen pyrolysis. This supports the catalytic effect of minerals on the degradation of kerogen in oil shale, which leads to the occurrence of coking and cracking reactions due to delay in vaporization temperature of hydrocarbons[186].

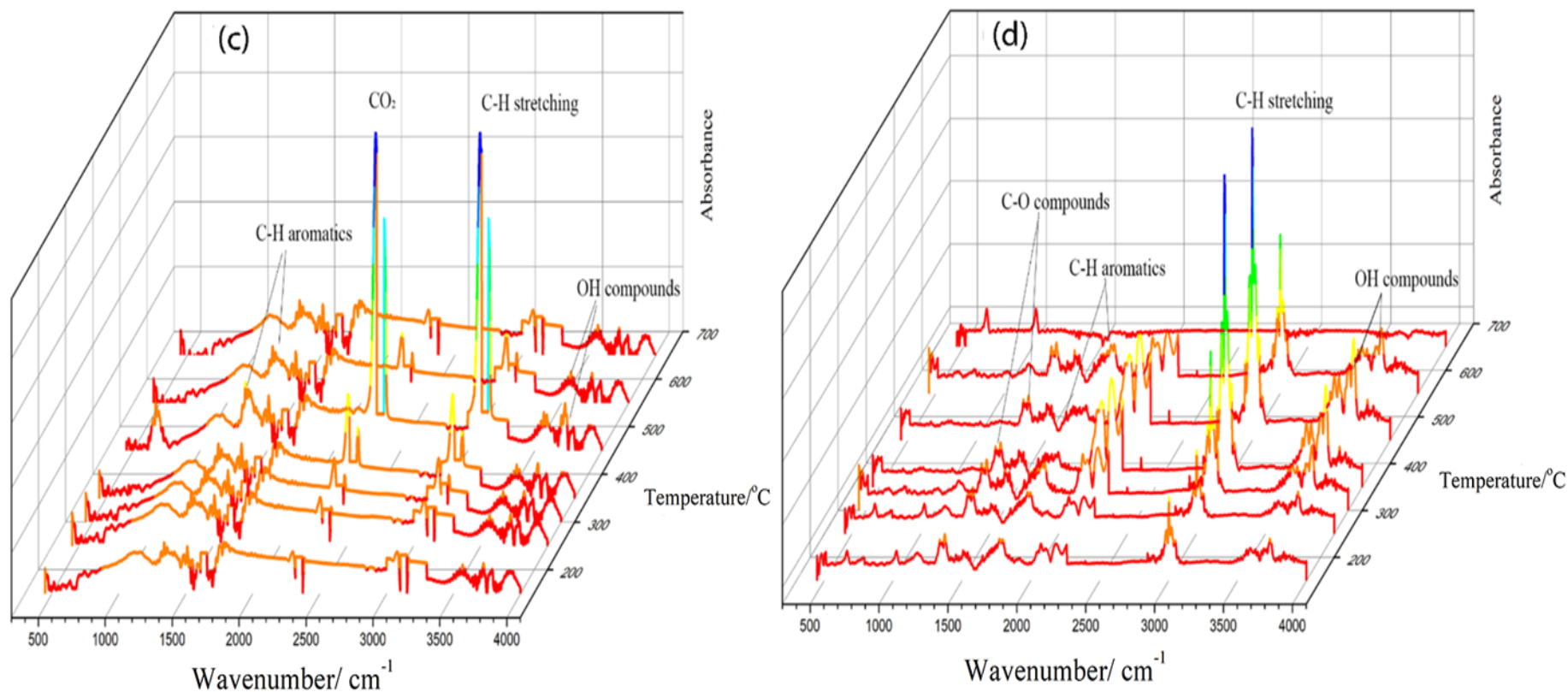


Fig 3.12. TG-FTIR spectra depicting different evolved compounds during pyrolysis of (a) oil shale (b) kerogen at $20^{\circ}\text{C}/\text{min}$.

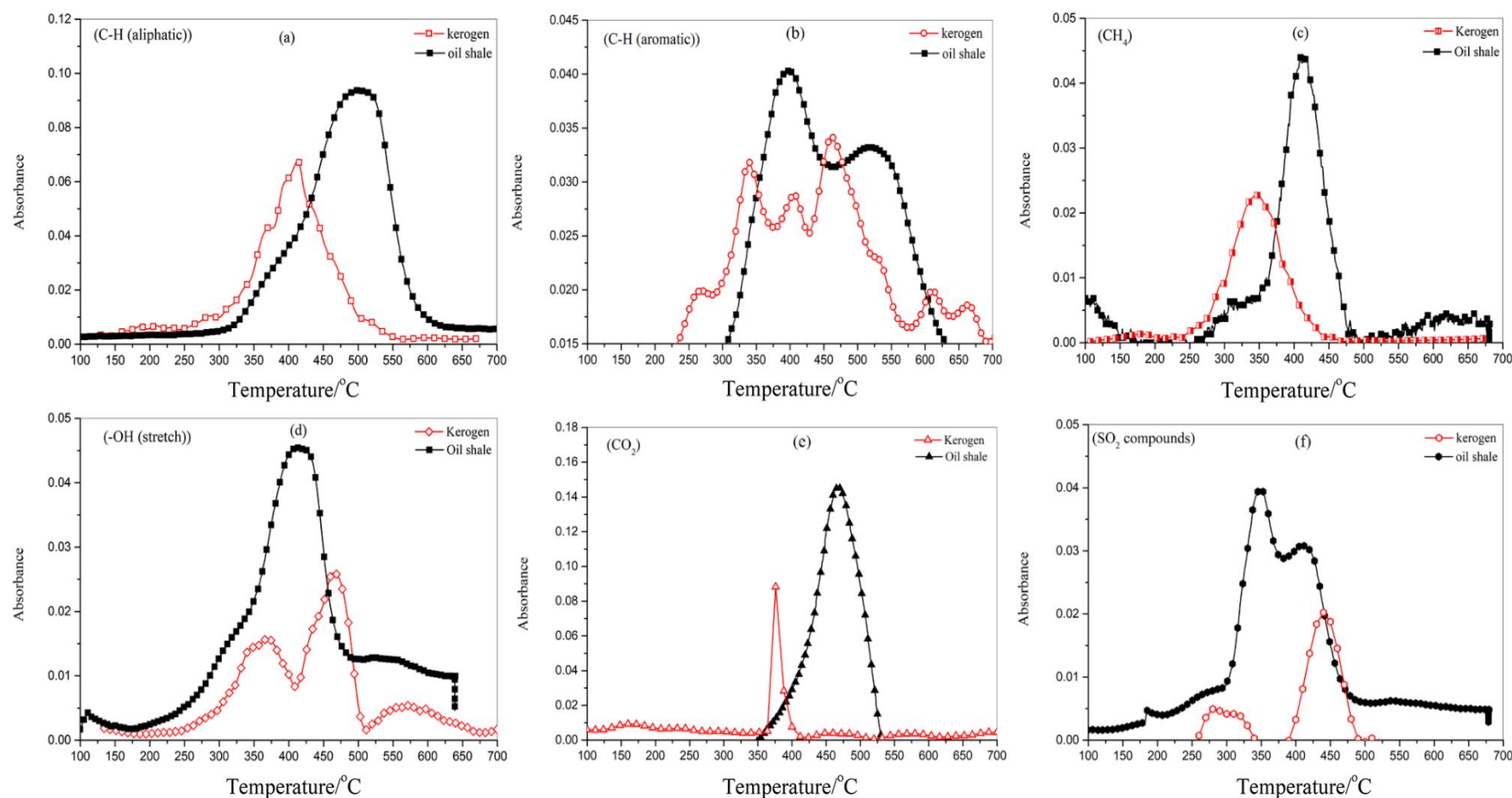


Fig 3.13. TG-FTIR spectra of evolved products during pyrolysis of oil shale and kerogen at 20°C/min (a) aliphatic compounds, (b) aromatic compounds (c) methane, (d) –OH compounds, (e) carbon dioxide and (f) S=O compounds.

3.7. Lab-scale pyrolysis experiments

3.7.1. Process optimization of oil shale pyrolysis using RSM

The methodology of the lab-scale pyrolysis process has been discussed in section 2.12.1. Optimization of the pyrolysis process was done using RSM with CCD model. The total number of experiments required for “n” number of parameters is given by the $2^n + 2n + c$ where c is number of centre point experiments. Three parameters were considered viz. heating rate (5 - 20°C/min), final temperatures (450-650°C) and particle size (0.150-12 mm). Five responses viz. mass conversion (mass loss during pyrolysis), oil yield, gas yield, aqueous phase (oil in water) and spent shale were selected corresponding to the parameters. The model suggested 20 experiments with 6 center points. The model predicted parameters and experimental generated data with model predicted data are shown in Table 3.11. The model predicted values vs actual or experimental values plot for each response is shown in Fig 3.14 (a-e). The significance of the data obtained from the model was evaluated from the p-value of the ANOVA equation corresponding to each response.

$$\text{Mass conversion (\%)} = 23.45 + 0.5845A + 4.73B - 1.33C + 0.1087AB + 0.0162AC - 0.2238BC - 0.8403A^2 - 2.43B^2 - 0.7007C^2 \quad (3.1)$$

$$\text{Oil yield (\%)} = 11.26 + 0.0450A + 3.07B - 1.40C + 0.2063AB - 0.2387AC - 0.8412BC - 0.9363A^2 - 1.17B^2 - 0.9064C^2 \quad (3.2)$$

$$\text{Gas yield (\%)} = 10.29 + 0.6364A + 1.44B + 0.6789C + 0.5200AB + 0.4675AC + 0.3975BC - 0.3278A^2 - 0.9890B^2 + 0.1808C^2 \quad (3.3)$$

$$\text{Aqueous phase (\%)} = 1.90 - 0.2969A + 0.1245B - 0.5569C - 0.1975AB + 0.0050AC - 0.3925BC - 0.5081A^2 - 0.2816B^2 - 0.0408C^2 \quad (3.4)$$

$$\text{Spent Shale (\%)} = 76.55 - 0.4848A - 4.59B + 1.43C - 0.3512AB - 0.0187AC - 0.0187BC + 0.7857A^2 + 2.43B^2 + 0.6461C^2 \quad (3.5)$$

Where, A = Heating rate (°C/min); B = Temperature (°C); C = Particle size (mm).

The significance of the parameters with respect to mass conversion is shown in Table 3.12. The ANOVA report of oil yield is tabulated in Table 3.13. The ANOVA of mass loss, gas yield, aqueous phase and spent shale are shown in Appendix (Table A1, A2, A3, and A4, respectively). RSM suggested F value of 19.72 and p – value of 0.0001 for mass conversion, F value of 13.81 and p value of 0.0005 for oil yield, F-value of 40.65 and p – value < 0.0001 for gas yield, F-value of 4.24 and p – value of 0.02 aqueous phase and F-value of 20.04 and p–value of 0.001 for spent shale. The F-value and p-values obtained suggests the values are significant and thus acceptable. Although all the parameters were found to be significant, the strength of significance varied for each parameter. For mass conversion, oil yield, gas yield and spent shale the p-value of the parameter “Temperature” was found to be <0.0001, which signifies it as the most significant variable. But the interaction of “Temperature” with other parameters were observed to be less significant. This establishes “Temperature” as the most influential parameter during pyrolysis of oil shale. For mass conversion, the statistically determined R² value for the fitted model was found to be 0.9596, which indicated that 95.96% of the experimentally obtained results showed consistency with the predicted data of the suggested model. Similarly, the R² values for oil yield, gas yield, aqueous phase and spent shale were noted to be 0.9395, 0.9786, 0.8278 and 0.9575 respectively. Aqueous phase showed the least consistency with the predicted data with convergence of 82.78%. The most desired yield was obtained at heating rate of 10 °C/min, temperature of 600 °C and particle size of 0.150 mm. The oil yield was observed to be low with low mass loss, at lower heating rates and lower temperatures. At higher temperatures and high

heating rates, the mass loss was observed to be higher but oil yield decreased. Detailed observation of the pyrolysis process is explained below. The optimum values of the responses were determined with respect to maximum mass conversion, maximum oil yield, low gas yield, low aqueous phase and minimum spent shale for the set of considered parameters. The optimum values were determined from the ANOVA model (eq (3.1), (3.2), (3.3), (3.4) & (3.5)) by numerical method. The model predicted an optimum mass conversion of 27.65%. From the total mass conversion, 14.56 % oil yield, 9.12 % gas yield and 2.97 % aqueous phase were obtained. Total spent shale which remained was 72.35 %. The surface plots showing the relation between the process variables and the obtained results are presented in Fig 3.15 (a-e) with the optimum points shown by the red dot in the response surface plots.

3.7.2. Observations of pyrolysis experiments

At 5°C/min and 600 °C with a hold time of 2 hours, the percentage of oil yield was found to be 13.25%. The first drop was observed at 350 °C, and the product collected at 350 °C was thick and waxy with a pale cream color. The wax production was observed till 500 °C, and from 500 to 600 °C, a dark black oil was collected. At 10 °C/min heating rate, the oil yield increased to 15.45% under the same operating conditions. Initially, a pale cream wax was produced in the temperature range of 352 °C to 500 °C. In the next phase of increasing temperature (525 to 600 °C), a dark black oil got collected over the wax. Increasing the heating rate from 10 to 20 °C/min, the oil yield decreased to 12.54% and the gas yield increased to 9.76%. The first drop of wax was observed at 425 °C. The production of dark black oil was observed after 500 °C and continued till 600 °C. It was observed from the pyrolysis process, optimum result with maximum oil percentage was observed at 10 °C /min at 600 °C. The pyrolysis runs conducted at 450 °C and 500 °C showed the production of thick wax for 5 °C/min and 10 °C/min, and for 20 °C/min the less viscous oil and

no dark black oil was collected. Performing the runs at 550 °C showed the production of both waxy and dark black oil phases for each heating rate with similar percentage of oil and gas products as in 600 °C. At 650 °C the total decomposition increased but oil production decreased and the production of gases increased. This may have occurred because of the secondary thermal cracking reactions [33, 208, 209]. The lab-scale pyrolysis experiments were triplicated to check for repeatability, and the quantification of yield obtained from the lab-scale pyrolysis of the oil shale sample with error percentage are shown in Fig 3.16. The oil sample obtained at the optimum condition showed GCV of 23 MJ/kg, with flash point of 40°C, and fire point of 45°C. The oil sample showed at pour point of 2°C, and residual carbon content of 0.5 wt/wt%.

3.7.3. Pyrolysis of isolated kerogen

The isolated kerogen samples were pyrolyzed in a lab-scale pyrolysis setup at 600°C at a heating rate of 10°C/min in the presence of nitrogen as the purge gas. The oil obtained from pyrolysis of extracted kerogen was compared with oil produced from pyrolysis of oil shale and solvent extracted bitumen using ¹H NMR analysis. In the present study, for the purpose of comparison the oil obtained at the optimum condition from pyrolysis of oil shale is termed as SO-1, the oil obtained from the pyrolysis of kerogen is termed as SO-2, and the bitumen extracted from the oil shale sample during isolation of kerogen is named as SO-3.

Table 3.11. Experimental design matrix with model suggested parameters and corresponding experimental responses.

Run	Heating Rate (°C/min)	Temperature (°C)	Particle Size (mm)	Mass Conversion (wt%)		Oil yield (wt/wt%)		Gas yield (wt/wt%)		Aqueous phase (wt/wt%)		Spent Shale (wt/wt%)	
				Actual	Predicted	Actual	Predicted	Actual	Predicted	Actual	Predicted	Actual	Predicted
1	25.11	550	5.12	23.88	22.06	9.78	8.69	10.89	10.43	3.21	2.84	76.12	77.96
2	20	650	10	26.46	23.37	8.35	9.08	12.87	13.29	1.24	1.56	77.54	76.28
3	20	450	0.15	15.23	16.32	4.45	5.82	6.73	7.08	3.05	2.81	84.77	83.53
4	5	450	10	12.06	13.15	3.65	5.02	7.06	7.41	1.35	1.11	87.94	86.70
6	10	600	0.15	27.33	23.45	10.23	11.26	10.56	10.29	2.54	1.90	76.67	76.50
7	10	600	0.15	27.65	23.45	14.56	14.05	9.12	10.29	2.97	1.90	72.35	76.55
8	10	600	13.32	21.05	19.23	7.43	6.34	12.4	11.94	1.22	0.85	78.95	75.13
9	5	650	10	21.75	21.95	9.66	9.06	10.07	10.04	2.03	2.54	78.25	83.56
10	10	550	5.12	23.21	23.45	10.97	11.26	10.27	10.29	1.97	1.90	76.79	76.55
11	5	450	0.15	15.02	15.40	5.63	5.67	7.88	7.78	3.07	3.02	83.6	83.56
12	20	650	0.15	26.25	26.45	14.65	14.05	10.23	10.20	1.37	1.88	73.75	73.69
13	10	720	5.12	24.32	24.54	12.34	13.10	10	9.91	1.98	1.31	75.68	75.70
14	10	550	5.12	23.78	23.45	11.3	11.26	10.47	10.29	2.01	1.90	76.22	76.55
16	5	650	0.15	25.72	25.09	13.25	13.07	8.79	8.83	2.87	2.87	74.84	75.13
17	10	380	5.12	10.68	8.63	4.64	2.79	5.44	5.07	0.6	0.89	89.32	91.13
18	10	550	5.12	22.97	23.45	11.09	11.26	9.99	10.29	1.89	1.90	77.03	76.55
19	10	550	5.12	23.45	23.45	11.25	11.26	10.24	10.29	1.96	1.90	76.55	76.55
20	20	450	10	12.22	14.14	3.27	4.22	8.29	8.58	0.66	0.92	87.78	86.20

Table 3.12. Analysis of variance table for the experimental design results of RSM for oil yield (%).

Source	Sum of squares	Degree of freedom (df)	Mean square	F value	p-value
Model	194.84	9	21.65	13.81	0.0005
A-heating rate	0.0177	1	0.0177	0.0113	0.9180
B-temperature	128.31	1	128.31	81.84	<0.0001
C-particle size	17.18	1	17.18	10.96	0.0107
AB	0.3403	1	0.3403	0.2171	0.6537
BC	0.4560	1	0.4560	0.2909	0.6043
AC	5.66	1	5.66	3.61	0.0939
A ²	6.57	1	6.57	4.19	0.0748
B ²	18.34	1	18.34	11.70	0.0091
C ²	6.16	1	6.16	3.93	0.0827
Residual	12.54	8	1.57		
Lack of fit	12.34	3	4.11	102.15	<0.0001
Pure error	0.2013	5	0.0403		
Corrected total	207.38	17			
Standard deviation		1.25	R ²		0.9395
Mean		9.14	Adjusted R ²		0.9015
Coefficient of variation (%)		13.70			

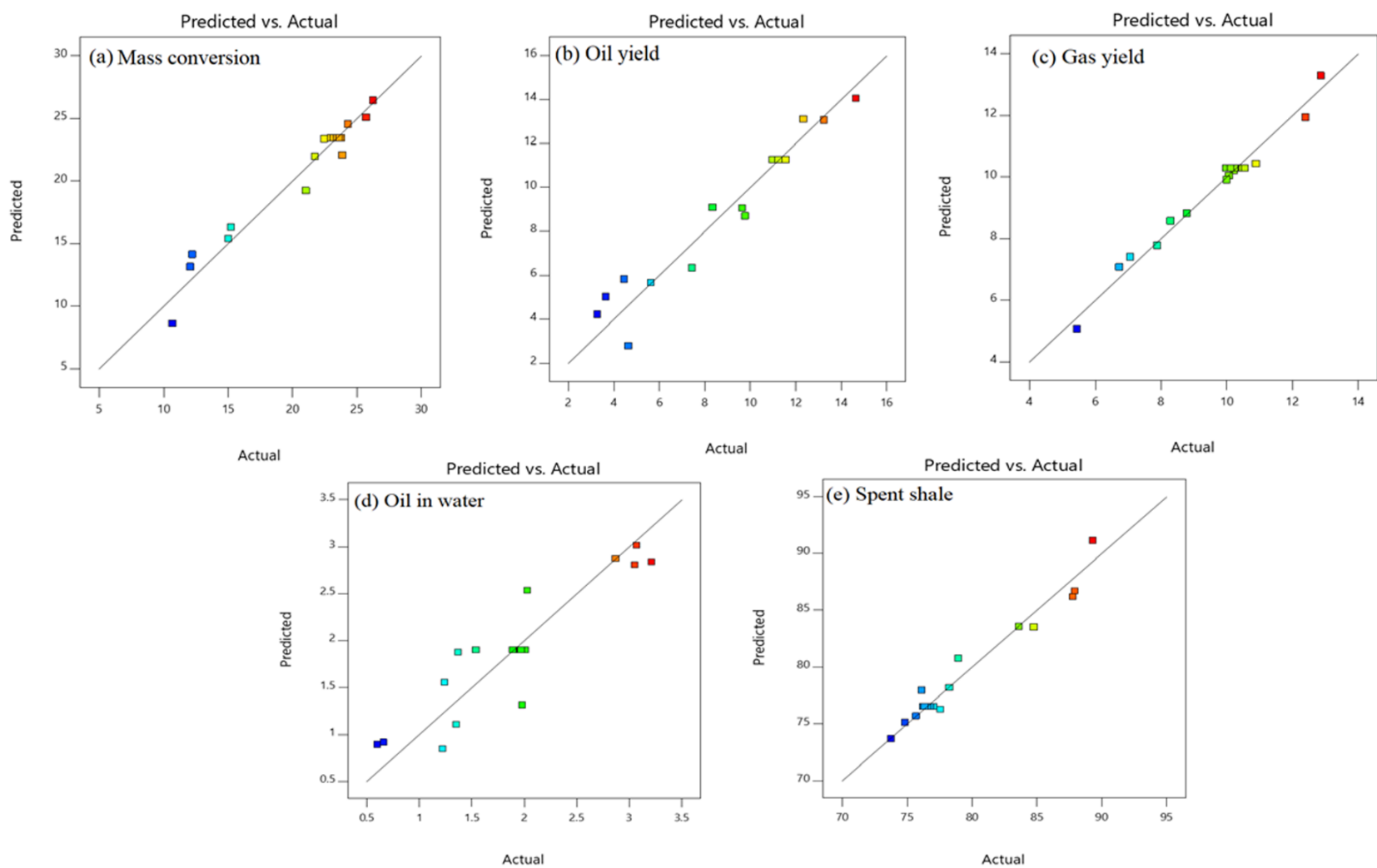


Fig 3.14. Predicted vs Actual value plot for (a) mass conversion, (b) oil yield, (c) gas yield, (d) aqueous phase, (e) spent shale.

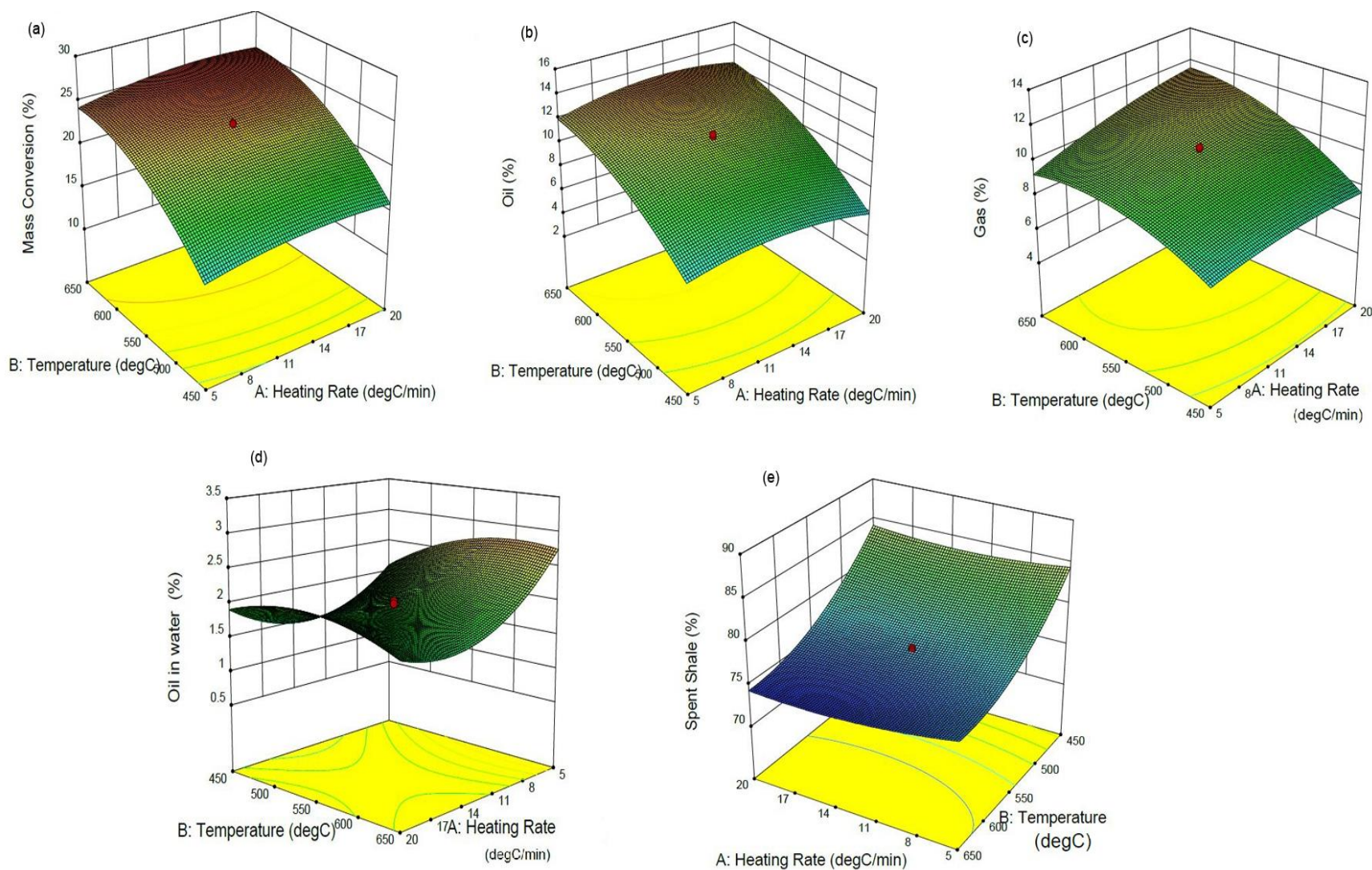


Fig 3.15. Effect of process parameters obtained for (a) mass conversion (b) oil (c) gas (d) aqueous phase & (e) spent shale.

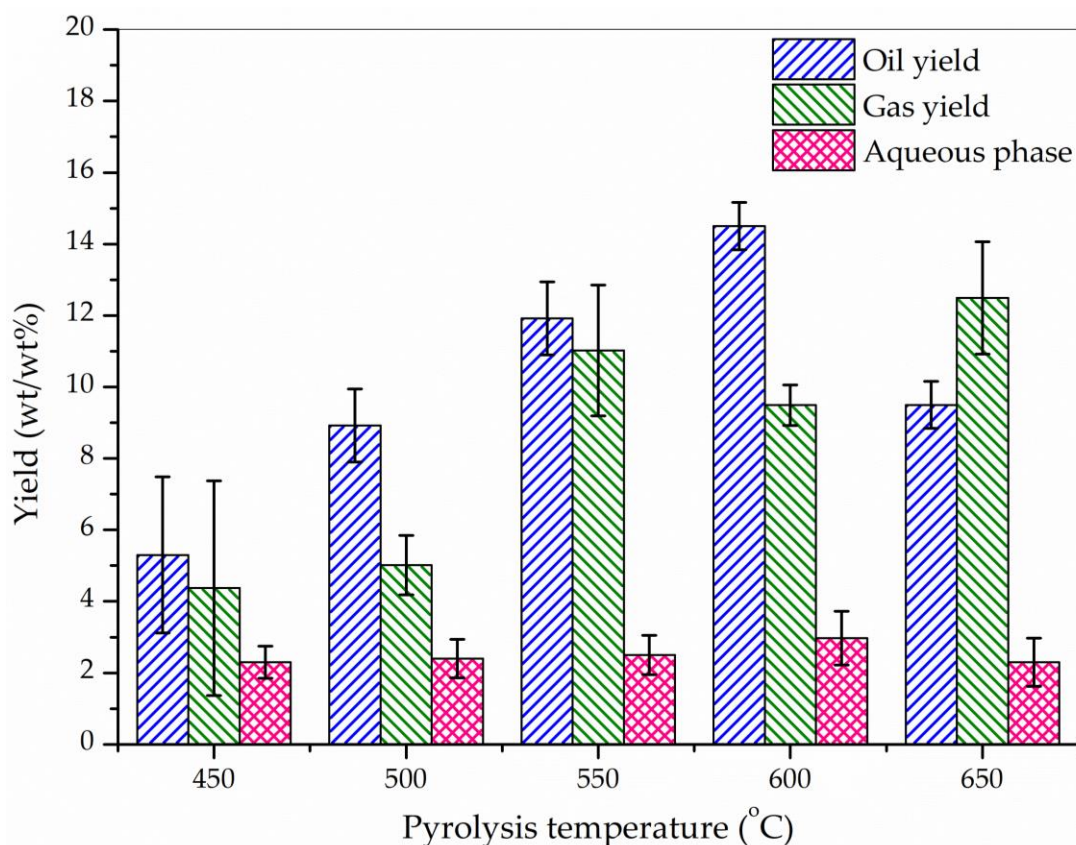


Fig 3.16. Distribution of yield from lab-scale pyrolysis at different pyrolysis temperature of 450, 500, 550, 600, and 650°C at a heating rate of 10°C/min, and holding time of 2 hours.

3.8.Characterization of gas sample

The gas samples were collected in Tedlar bags periodically at different reactor temperature values of 300, 350, 450, 550, 600, and 650°C during the pyrolysis process and at a heating rate of 10 °C/min, and 0.150 mm particle size. The composition of the permanent and hydrocarbon gases identified by GC-TCD and GC-FID analysis. The pyrolytic gases obtained during the lab-scale pyrolysis experiment of oil shale showed the presence of permanent gases such as hydrogen (H₂), carbon monoxide (CO) and carbon dioxide (CO₂), and hydrocarbon gases from carbon number C₁ to C₅. The relative concentration of the identified permanent and hydrocarbon gases is presented in Fig 3.17 and Table 3.13. For the gas samples obtained from pyrolysis of oil shale, the concentration of CH₄ decreased with increase in pyrolysis temperature from 300°C to 550°C, and

increased from 550°C to 650°C. during pyrolysis of OS, the concentration of CO and CO₂ increased 350°C to 450°C, increased from 450°C to 650°C. The concentration of C₂ hydrocarbon gases decreased from 350°C to 550°C, and decreased from 550°C to 650°C. C₃, C₄, and C₅ gases increased from 350°C to 550°C, and decreased from 550°C to 600°C. However, it was observed that C₃, C₄, and C₅ gases were absent at pyrolysis temperature of 650°C.

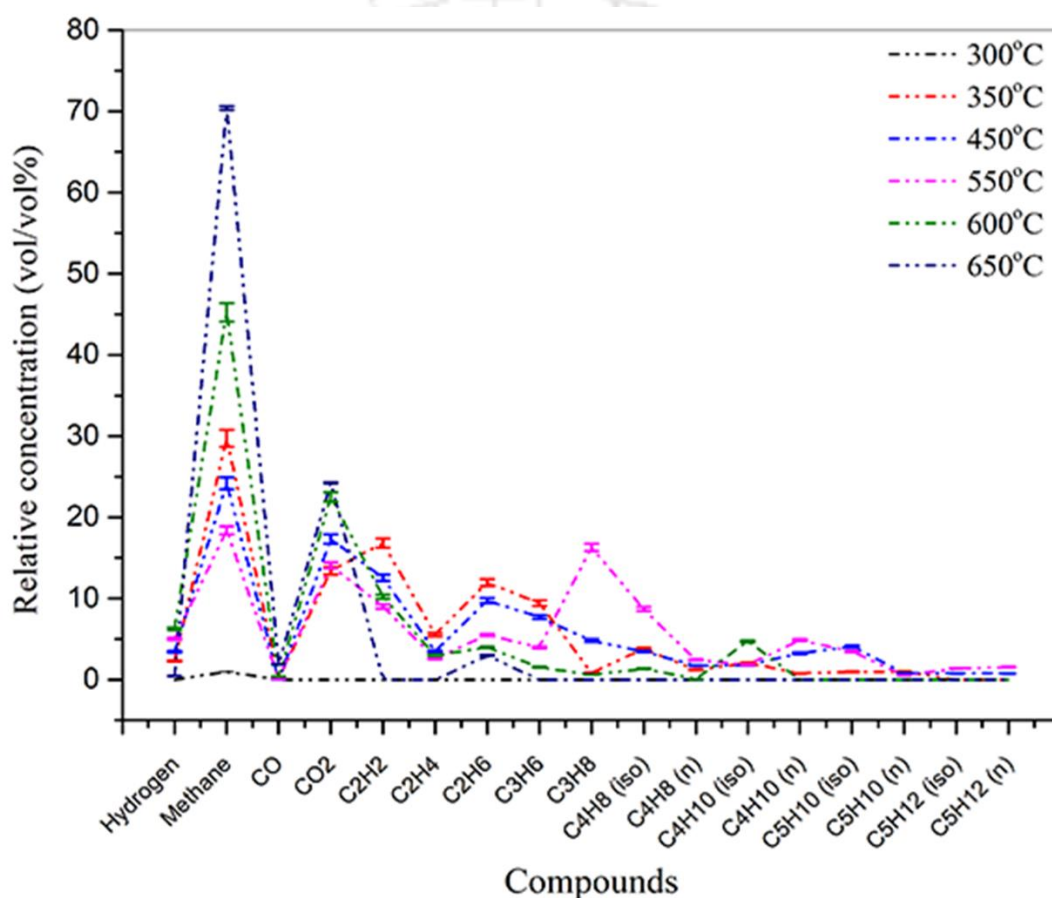


Fig 3.17. Relative concentration of permanent and hydrocarbon gases produced during pyrolysis of oil shale sample for particle size of 0.150 mm, at heating rate of 10°C/min, and up to pyrolysis temperature of 650°C.

Table 3.13. Mean relative concentration (vol/vol %) of permanent and hydrocarbon gases collected at different temperatures during pyrolysis at heating rate of 10°C/min, and particle size of 0.150 mm.

Compounds	Pyrolysis Temperature (°C)					
	300	350	450	550	600	650
H ₂ (%)	-	2.29	3.44	5.05	6.27	0.46
CH ₄ (%)	-	29.72	28.69	23.4	45.23	70.42
CO (%)	-	0.14	0.03	0.14	0.4	1.9
CO ₂ (%)	-	21.42	19.61	28.36	22.51	24.26
C ₂ H ₂ (%)	-	10.84	8.55	9.03	10.24	0
C ₂ H ₄ (%)	-	5.54	3.48	3.6	3.01	0
C ₂ H ₆ (%)	-	5.96	5.76	6.53	3.99	3.01
C ₃ H ₆ (%)	-	5.43	7.71	4.97	1.55	0
C ₃ H ₈ (%)	-	0.85	5.82	6.49	0.62	0
C ₄ H ₈ (iso)(%)	-	3.81	3.46	3.7	1.36	0
C ₄ H ₈ (n)(%)	-	1.22	1.74	3.43	0.08	0
C ₄ H ₁₀ (iso)(%)	-	2.07	1.81	1.82	4.74	0
C ₄ H ₁₀ (n)(%)	-	0.77	5.25	2.87	0	0
C ₅ H ₁₀ (iso)(%)	-	0.97	1.09	0.49	0	0
C ₅ H ₁₀ (n)(%)	-	0.95	0.82	0.51	0	0
C ₅ H ₁₂ (iso)(%)	-	0	0.28	0.19	0	0
C ₅ H ₁₂ (n)(%)	-	0	0.38	0.27	0	0

3.9. Characterization of oil sample

3.9.1. Gas chromatography- Mass spectrometry

The GC-MS spectra of the pyrolytic oil sample (SO-1) obtained at 10 °C/min, 600 °C and 0.150 mm particle size is shown in Fig 3.18 (a). The compounds identified at different retention times and their area percentage are summarized in Table 3.14 and the quantification of the identified products according to their functional groups are shown Table 3.15. The carbon number of the compounds constituting the oil sample ranged from C₆ to C₃₈. The analysis showed the area percentage of aliphatic compounds to be 51.29% and the aromatic compounds of 28.66%. As reported earlier, the shale oil from the oil shales of Upper Assam and Arunachal Pradesh were more dominant in aromatic compounds with a maximum of 64.3% by mass [10]. The difference in the aromatic percentage might be because of the site of collection of oil shale sample. The production of wax during pyrolysis illustrates the presence of paraffin compounds which are aliphatic in nature [210]. Also, the GC-MS showed the presence of saturated aliphatic compounds to constitute 38.29% of total aliphatic compounds. The aromatic compounds were phenols, naphthalenes and asphaltenes. Oxygen containing compounds such as ethers, esters, alcohols and acids constitute 18.76% of the total area percentage. Quantity of organic sulfur was found to be 2.060%. The GC-MS analysis shows the shale oil to be aliphatic in nature. The Upper Assam shale oil shows similarity to the shale oil obtained from Huadian oil shale which has aliphatic percentage of 57% [211].

3.9.2. Nuclear magnetic resonance (¹H NMR) spectroscopy

¹H spectroscopy results identified the chemical shift of the proton (¹H) and carbon compounds of the produced shale oil at 10 °C/min, 600 °C and 0.150 mm particle size. The ¹H NMR spectra is presented in Fig 3.18(b). Quantification of the chemical shift with respect to mass percentage and

comparison with crude oil is shown in Tables 3.16. For ^1H NMR, the integral area showed 36% alkanes, 29% unsaturated aliphatics and α -heteroatoms. Methoxy and carbohydrates of 10%, aromatics of 21% and 1% esters and carboxylic acid. Comparison of the composition of the pyrolytic shale oil with of Assam crude oil obtained from literature [212], showed the similarity in the concentration of Aliphatic compounds. Percentage of aromatic compounds were found to be more in shale oil (21-29%) compared to 3-8% in the Assam crude oil.

The pyrolytic oil sample obtained at the optimum condition (SO-1) was compared with the oil obtained from pyrolysis of kerogen (SO-2), and the solvent extracted bitumen (SO-3) by using ^1H NMR analysis to study the trend of evolution of products due to degradation of kerogen inside the oil shale and in the presence of inherent mineral matters, and the contribution of inherent bitumen to the composition of the pyrolytic oil, during the degradation of kerogen.

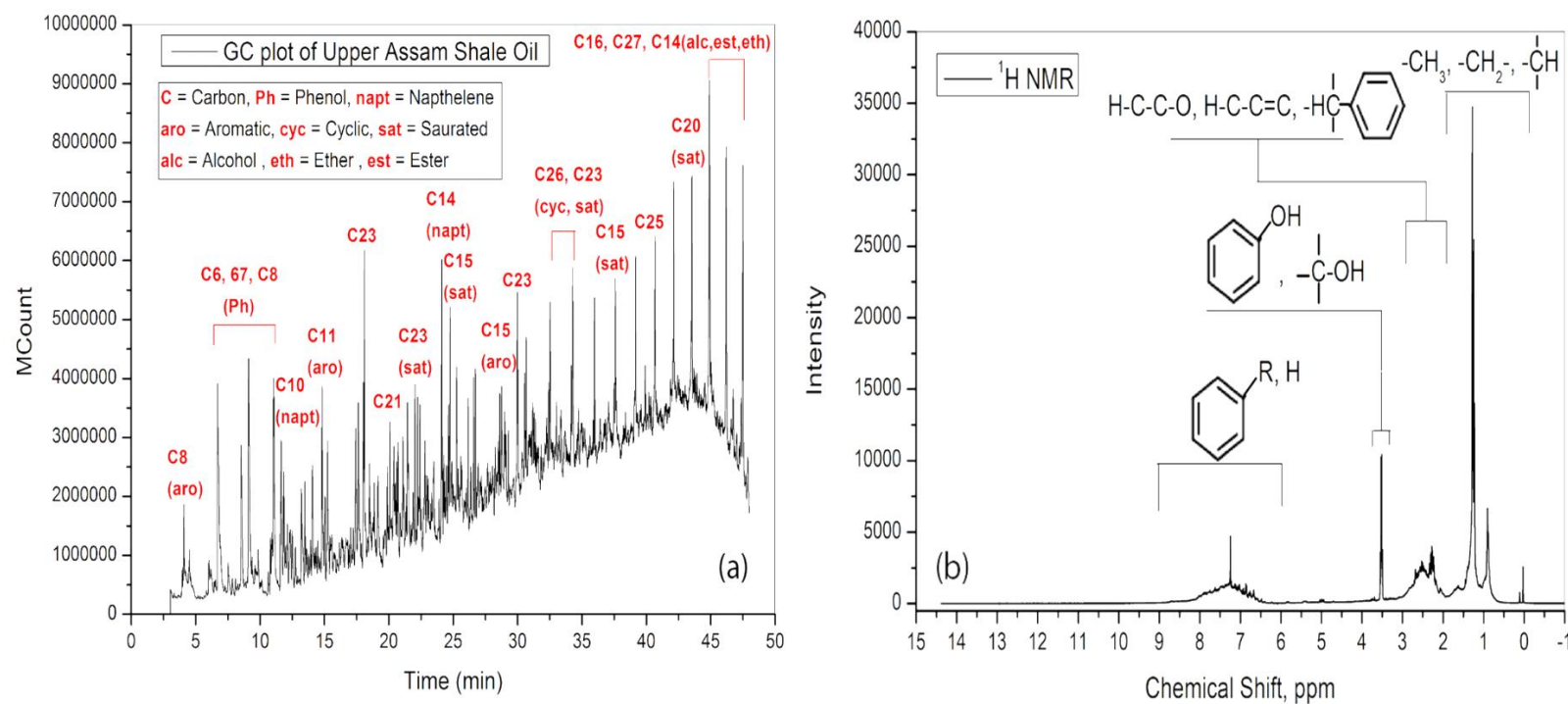


Fig 3.18. (a) GC peaks allocation from GC-MS analysis, and (b) ^1H NMR of Upper Assam shale oil obtained from pyrolysis at $10^\circ\text{C}/\text{min}$, 600°C and 0.150 mm particle size.

Table 3.14. Chemical compounds detected in Upper Assam shale oil by GC-MS.

Sl. No.	Compound	Retention Time	Molecular Weight	Area %
1	p-xylene	4.08	106	0.61
2	Phenol	6.71	94	1.083
3	Phenol, 2-methyl-	8.54	108	1.63
4	Phenol, 3, 4-dimethyl-	11.06	122	3.79
5	Napthalene	11.84	128	1.44
6	7-tetradecane	12.12	196	0.66
7	2-butyloctanol	12.35	186	1.27
8	Phenol, 2,3,6-trimethyl-	12.50	136	1.89
9	2-(2-hydroxyphenyl)buta, 1,3-diene	12.74	146	0.92
10	Indine, 1-ethylindene	14.81	141	1.89
11	Benzocycloheptatetraene	15.24	142	2.00
12	10 – Heneicosane (c,t)	17.42	294	2.34
13	4-methyldocosane	19.14	324	1.37
14	1-Nonadecane	19.89	266	0.89
15	1-Docosene	22.23	308	1.19
16	1-Methylnonadecane	22.41	282	1.10
17	Dodecane, 2,6,10-trimethyl-	22.80	212	2.12
18	9-Nonadecane	24.75	266	2.45
19	Nonadecane	26.58	268	1.34
20	Anthracene, 2-methyl-	26.73	192	1.47
21	1-Tricosene	28.60	322	1.09
22	10-methylnonadecane	30.55	282	1.36
23	6-octadecanoicacid, methyl ester (Z)	30.66	296	1.52

24	1,1-di(4-methylcyclohexyl)dodecane	32.53	362	1.95
25	Heptadecane, 9-hexyl-	34.17	322	1.34
26	Heptadecane	34.28	240	2.96
27	1-Decanol, 2-hexyl-	35.96	242	1.60
28	Heptacosane	37.60	380	1.83
29	1-Dodecanol, 2-hexyl-	39.15	270	1.41
30	2-Methyltetracosane	40.67	352	1.51
31	2-Ethyl dodecanol	42.12	214	1.88
32	Sulfurous Acid, hexyl pentadecyl ester	43.53	376	2.06
33	Hexadecane,1-(ethenyl-oxy)	46.20	268	3.65
34	2-ethyl, 1-dodecanol	47.49	214	3.928

Table 3.15. Composition summary of Upper Assam shale oil obtained at 10°C/min, 600 °C and 0.150 mm particle size by GC-MS analysis.

Compounds	Relative percentage (%)
Aromatic	28.66
Saturated aliphatics	38.29
Unsaturated aliphatics	12
Oxygen compounds	18.72
Organic Sulfur	2.06

Table 3.16. Mass percentage of compounds detected by ^1H NMR spectroscopy for Upper Assam shale oil obtained at $10^\circ\text{C}/\text{min}$, 600°C , 0.150 mm particle size and comparison with crude oil.

Proton Assignment (^1H)	Chemical Shift, ppm	Upper Assam Shale Oil (%)	Crude Oil (%) [208, 212]
Alkanes	0.5-1.5	36	67
Aliphatics α -heteroatoms or unsaturations	1.5-3	29	17
Alcohols, ring joined methylene	3-4.5	10	2
Methoxys and carbohydrates	4.5-6	3	3
Aromatic	6-8.5	21	8
Esters and carboxylic acids	8.5-10	1	2

3.9.3. ^1H NMR analysis of oil from pyrolysis of pure kerogen, extracted bitumen and comparison with oil obtained from pyrolysis of oil shale

^1H NMR spectra of the oil samples obtained by pyrolysis of oil shale (SO-1), oil obtained from pyrolysis of kerogen (SO-2), and solvent extracted bitumen (SO-3) are shown in Fig 3.19 (a-c). The initial calculation of the integral areas of different functional groups showed 36%, 21%, and 20% alkanes (0-1.5 ppm) and 29%, 16%, and 30% of aliphatics α -heteroatoms (1.5-3 ppm) in SO-1, SO-2, and SO-3 samples respectively. The samples showed a dominance of methylene hydrogen from 0.5 to 1.5 with a sharp peak at 1.25 ppm. The peaks occurring from 1.5 ppm to 1.8 ppm for SO-2 and SO-3 may correspond to naphthenic β hydrogen to aromatic rings. The percentage of α -methyl to aromatics was found to be 10%, 13%, and 15% in SO-1, SO-2, and SO-3, respectively. A small percentage of carbohydrates and methoxys were detected as 3%, 9%, and 4% in SO-1, SO-2, and SO-3, respectively. The oil obtained by pyrolysis of pure kerogen (SO-2) showed a high percentage of aromatics (35%) from 6.5-9 ppm, compared to 22% in oil obtained from pyrolysis of oil shale (SO-1) and 31% in solvent extracted bitumen (SO-3). The oil obtained by pyrolysis of pure kerogen (SO-2) and oil obtained from pyrolysis of oil shale (SO-1) showed 6% and 1% ester and carboxylic acids. It was observed that oil obtained from pyrolysis of oil shale (SO-1) and

solvent extracted bitumen (SO-3) contained a high percentage of naphthenic β hydrogen to aromatics and aliphatic α -heteroatoms compared to oil obtained by pyrolysis of pure kerogen (SO-2). But, SO-2 showed a relatively high percentage of aromatic compounds compared to SO-1 and SO-3. The high percentage of naphthenic β hydrogen in SO-1 may have occurred due to the coking of aromatic rings and branching due to the catalytic effect of minerals in oil shale. The total group molecular weight of the oil samples (T_w), total group molecular weight of aromatic compounds (A_w), and the total aromatic content (A_c) were calculated using the co-relations provided by Kumar et al.[10]. The quantification of the functional groups, T_w , A_w , and A_c with standard deviation are presented in Table 3.17. The total group molecular weights of SO-1, SO-2, and SO-3 samples were found to be 1489 g/mol, 1053.8 g/mol, and 1594 g/mol respectively. The total group molecular weight of aromatics was calculated as 335 g/mol, 450 g/mol, and 485 g/mol in SO-1, SO-2, and SO-3 samples respectively. The total aromatic content values were determined as 22.4 wt% (SO-2), 35.8 wt% (SO-1), and 30.4 wt% (SO-3). This showed that the hydrocarbons produced from kerogen contain a higher concentration of aromatic compounds before their interaction with the mineral matter present in the oil shale. Comparison of ^1H NMR data between solvent extracted bitumen and oil obtained by pyrolysis of kerogen showed a similar concentration of aromatics and α -methyl to aromatics. However, solvent extracted bitumen showed a much higher concentration of α -heteroatoms compared to oil obtained by pyrolysis of kerogen. Thus, it can be assumed that parts of kerogen initially mature into bitumen inside the oil shale[131], and the remaining kerogen and bitumen degrades simultaneously along with the mineral matter following multiple parallel reactions to form oil and gas[213]. The subsequent degradation of minerals (calcite and alkali earth metals present in the oil shale) leads to the coking of aromatic compounds in the evolved hydrocarbons and decreasing the total aromatic content in the shale oil[214].

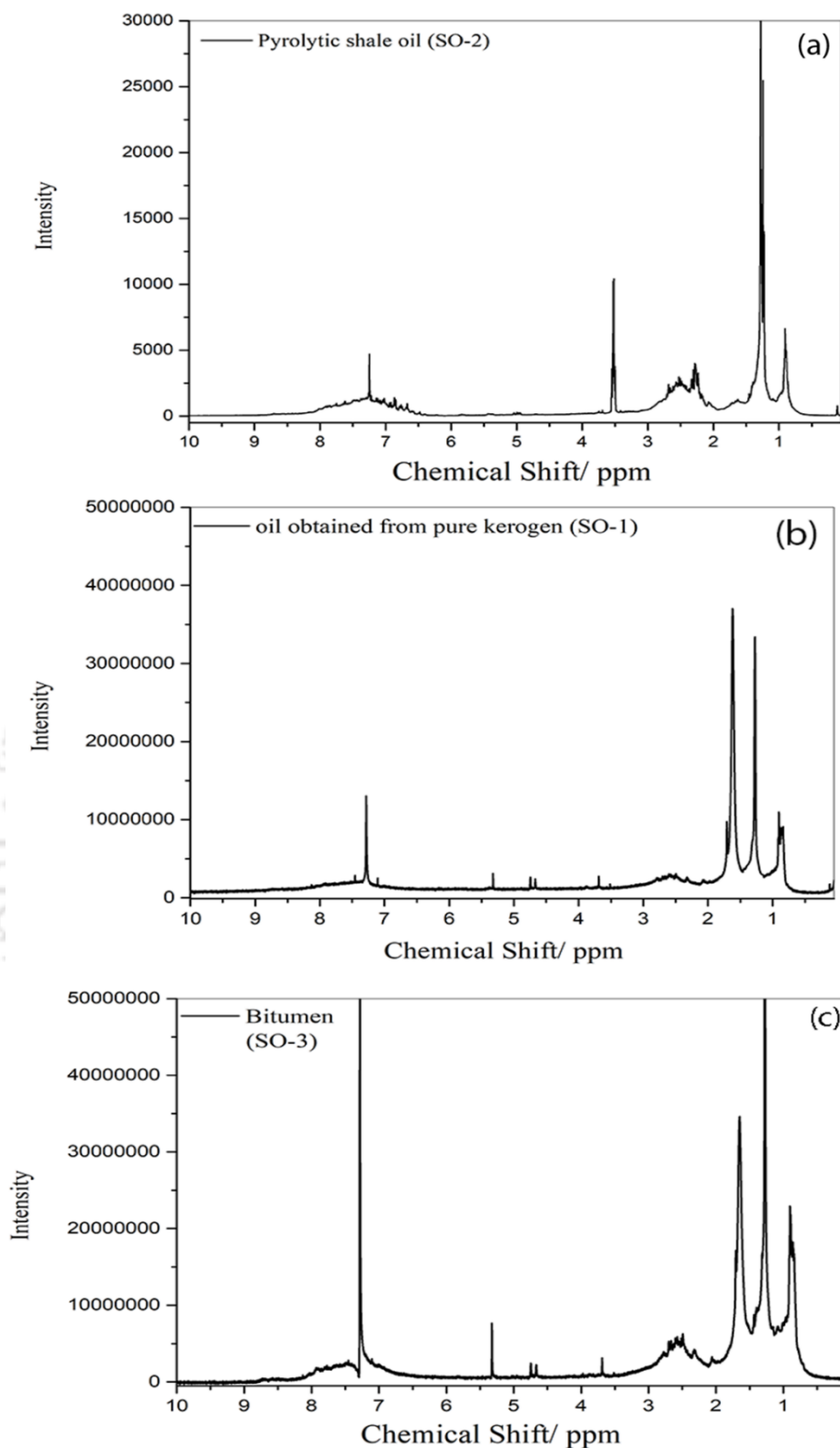


Fig 3.19. ^1H NMR spectra of (a) oil samples obtained by pyrolysis of oil shale (SO-1), (b) oil obtained from pyrolysis of extracted kerogen (SO-2), and (c) solvent extracted bitumen (SO-3).

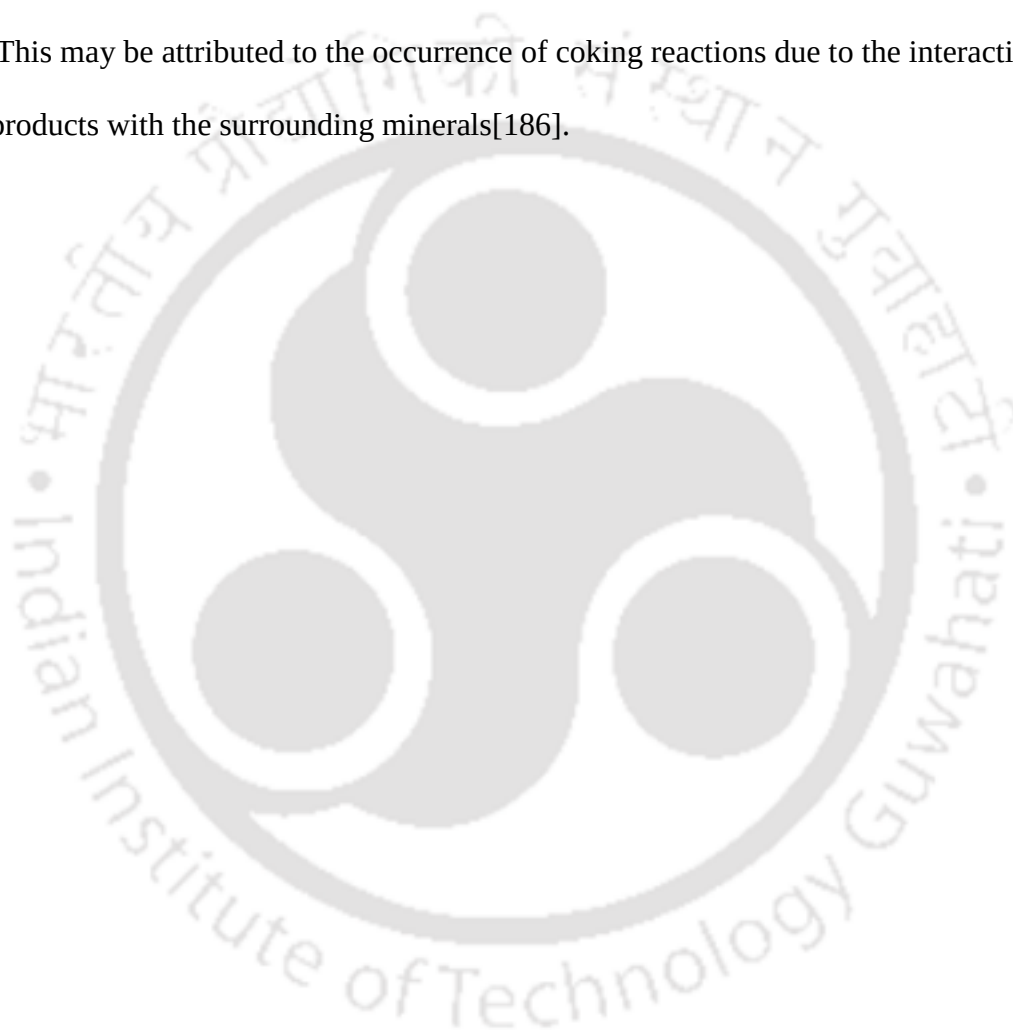
Table 3.17. NMR quantification of oil obtained by pyrolysis of pure kerogen (SO-2), oil obtained from pyrolysis of oil shale (SO-1), and solvent extracted bitumen (SO-3).

Proton assignment/parameters	SO-2	SO-1[22]	SO-3
Alkanes or methyl hydrogen (0.3-1.9 ppm)	36	30	34
Aliphatics α -heteroatoms or unsaturation (1.9-3 ppm)	29	7	16
α -Methylene to aromatic (3-4.5 ppm)	10	13	15
Methoxys and carbohydrates (4.5-6 ppm)	3	9	4
Aromatic (6-8.5 ppm)	21	35	31
Esters and carboxylic acids (8.5-10 ppm)	1	6	0
Total group molecular weight of sample (g/mol)	1489	1254	1594
Total group molecular weight of aromatic (g/mol)	335	450	485
Total aromatic content (wt %)	22.4	35.8	30.4

3.10. Microscopic study of kerogen and oil shale degradation mechanism

To better understand the degradation mechanisms of kerogen and oil shale as identified by the kinetic study, the entire degradation process of kerogen inside the oil shale sample was observed by performing a microscopic study (Fig 3.19). Oil shale sample of size 0.5 cm x 0.8 cm (43.318 mg) was scanned to identify the kerogen surrounded by mineral matter on its surface. The surface of the sample was illuminated using green fluorescence light. The organic matter appeared as a black stripe, and the minerals surrounding appeared in bright orange, with reflectance at certain sites. The reflecting or shining minerals may attribute to the silica minerals and moisture on the surface of the oil shale sample. To study the thermal degradation process, the sample was heated non-isothermally (at 10°C/min) to 100, 200, 350, and 600°C in an inert nitrogen environment at a flow rate of 40 ml/min for different durations. The samples were allowed to cool inside the reactor, and the cooled sample was weighed and viewed under the microscope for changes in surface morphology. In the first step, the sample was held at 100°C for 24 hours to mimic the pre-drying process. Around 0.2% weight loss was observed corresponding to moisture loss. No noticeable change was observed in the morphology of the kerogen or the surrounding minerals. The sample was further heated to 200°C for 24 hours, which was observed as the onset temperature of the evolution of compounds during kerogen degradation by thermogravimetric analysis (Fig 3(a-f)). At this temperature, a minute weight loss of 0.02% was observed, and kerogen trapped in the fracture appeared to expand as an indication of the initiation of kerogen swelling[21]. The initially observed reflectance of the minerals began to disappear. This may have occurred due to the removal of moisture from the surface and inbound in certain clay minerals[22, 25]. Following this, the sample was again heated in the pyrolysis reactor at 350°C for 6 hours. At this temperature, 1% weight loss was observed, and the organic matter had spread outside the fissure and accumulated

around the fractures and pores on the surface of the oil shale sample. This shows the maturation of kerogen into oil and bitumen. The sample was further pyrolysed at 600°C for 6 hours. At 600°C the entire surface morphology of the oil shale sample changed with an additional weight loss of 2.5%. The fracture and pores previously containing the kerogen appeared to be hollow, some amount of organic matter in the form of coke was found to be conformed to the walls of the fracture. This may be attributed to the occurrence of coking reactions due to the interaction of the evolved products with the surrounding minerals[186].



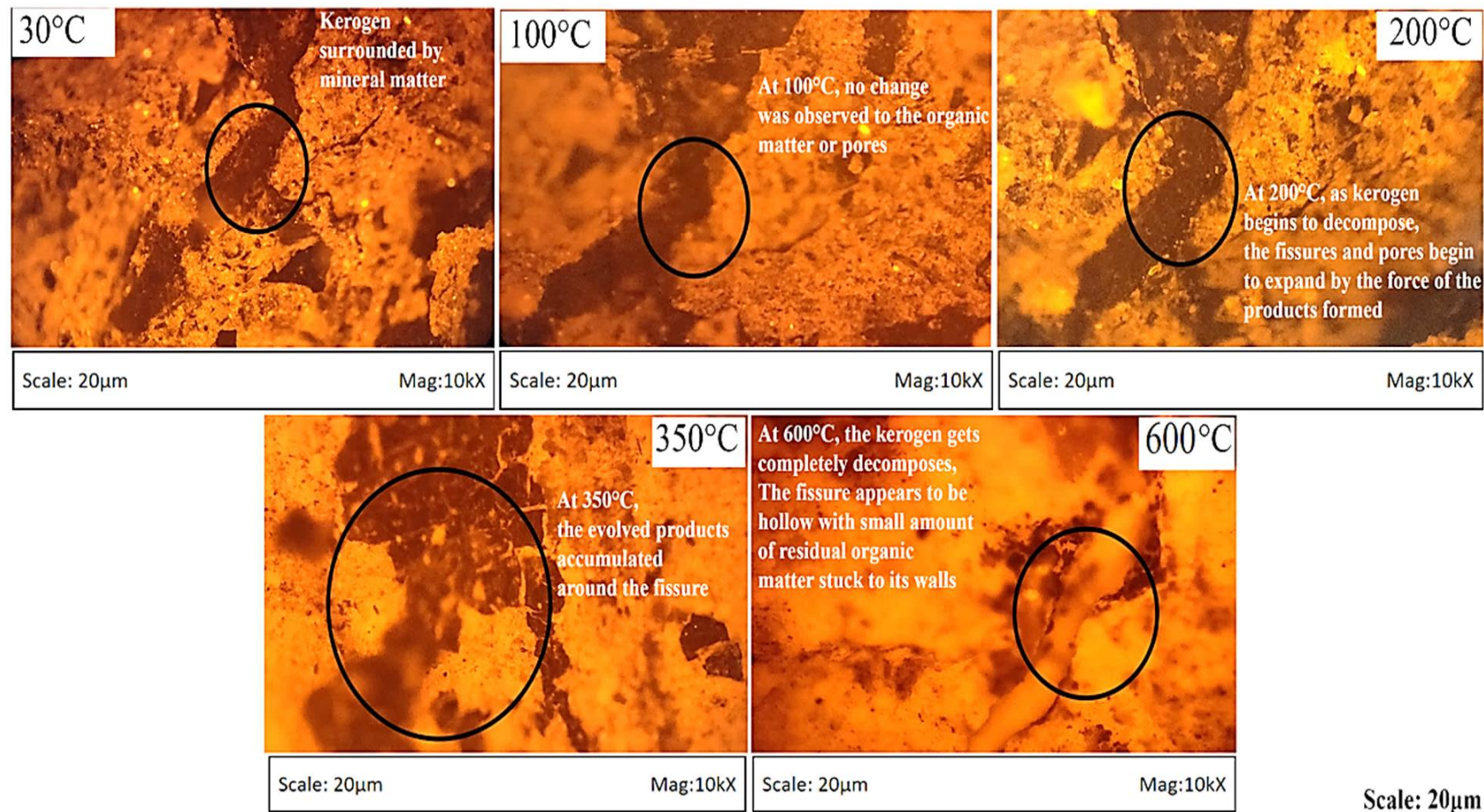


Fig 3.20. Microscopic images of oil shale kerogen samples during pyrolysis at temperature values of 30, 100, 200, 350, and 600°C depicting the thermal degradation mechanism of kerogen inside the fractures and pores of oil shale with increase in pyrolysis temperature.

3.11. Conclusive summary

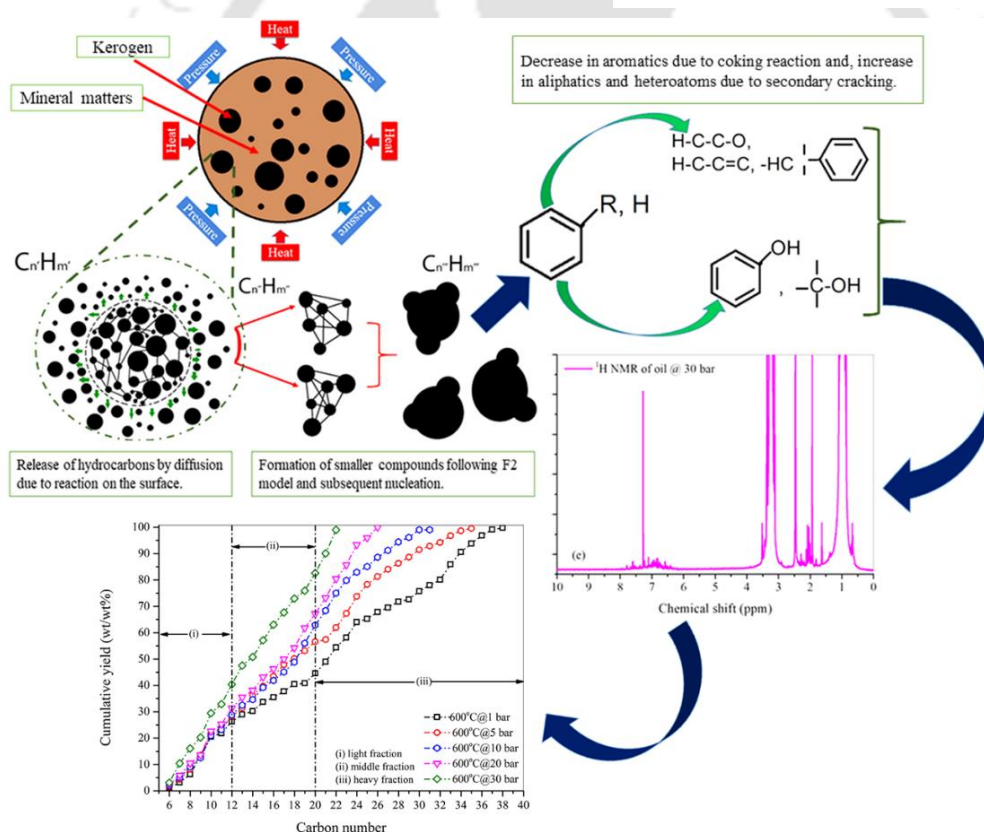
Physicochemical characterization showed the Indian oil shale sample to be of siliceous type. Thermogravimetric analysis of the oil shale sample showed a total organic matter content of 21%. Kerogen extracted from Indian oil shale by acid-solvent demineralization process was found free of mineral matter. The extracted kerogen sample was identified to be of type-II using Rock-Eval analysis. Kinetic study of the pyrolysis of kerogen estimated mean apparent activation energy values of 236 kJ/mol (AIC method), 230 kJ/mol (Friedman method), and 219 kJ/mol (Starink method). The extracted kerogen sample exhibited similar mean apparent activation energy compared to oil shale (245.6 kJ/mol), considering error percentage. The entire kerogen degradation process followed two reaction models viz. first-order reaction (F1 model) followed by A2 Avrami Eroffev nucleation reaction of produced hydrocarbons. The overall kinetic study demonstrated the swelling of kerogen on heating, followed by breakdown for generation of hydrocarbons and eventual nucleation of the produced hydrocarbons. TG-FTIR analysis showed the generation of hydrocarbons from kerogen begins around 200°C, compared to 300°C for oil shale samples at a heating rate of 20°C/min. Comparison of TG-FTIR analysis of extracted kerogen and oil shale pyrolysis showed the occurrence of cracking and coking reaction due to the delay in vaporization temperature of hydrocarbons in the presence of inherent minerals. Optimization of lab-scale pyrolysis process parameters showed maximum oil yield of 14.56 % was obtained at pyrolysis temperature of 600°C, at heating rate of 10°C/min and particle size of 0.150 mm with a holding time of 2 hours at final temperature. GC-MS and NMR characterization of the produced oil sample showed 58.13% aliphatic, 24.83% aromatics, with 17.04% heteroatomic compounds. ¹H NMR analysis of oil obtained from pyrolysis of kerogen, oil shale, and solvent extracted bitumen showed cracking and coking of produced hydrocarbons due to catalytic effect of minerals during simultaneous degradation of kerogen and mineral matter in oil shale. The occurrence of coking

reaction was observed by the reduction in aromatic content in the oil produced from oil shale pyrolysis. The microscopic study revealed that the thermal degradation of kerogen occurs inside the pores of the oil shale, and the generated products tend to escape through the apertures on the surface of the oil shale, and the occurrence of coking reaction of the produced hydrocarbons on the surface of the oil shale. This illustrates the event of D3 diffusion and A2 Avrami Eroffev nucleation model in the oil shale pyrolysis process. Therefore, the study of the degradation mechanism of kerogen emerges as a pathway into an integrated and better understanding of oil shale pyrolysis kinetics and optimization and design of efficient pyrolysis process.

Chapter 4

Effect of high-pressure on non-isothermal pyrolysis kinetics of oil shale and product yield

- High-pressure thermogravimetric analysis
- Kinetic study
- Isoconversional methods
- Lab-scale high pressure pyrolysis
- Simulated distillation



Published as:

Baruah, B., Tiwari, P. 2020. Effect of High Pressure on Nonisothermal Pyrolysis Kinetics of Oil Shale and Product Yield. *Energy & Fuels*, 34(12), 15855, 2020.

4. High-pressure pyrolysis

After establishment of the process kinetics and significant pyrolysis process parameters for the maximizing the oil yield from oil shale pyrolysis, the oil shale samples were subjected to High-pressure pyrolysis to investigate the effect of pressure on the pyrolysis process kinetics, yield and composition. Oil shale pyrolysis process is significantly influenced by pyrolysis temperature, heating rate, and pyrolysis pressure. The increase in pyrolysis pressure increases the hydrocarbon volatilization temperature and decreases the rate of vaporization of oil leading to delay in hydrocarbon expulsion and occurrence of cracking and secondary reactions. This phenomenon is well observed by the distribution of the kinetic parameters[63, 64].

This chapter presents a detailed kinetic investigation of pyrolysis of Indian oil shale under isobaric pressure using model-free isoconversional methods, followed by high-pressure lab-scale pyrolysis and characterization of pyrolytic oil and gases. The high-pressure thermogravimetry analyses were performed using a well-controlled, state of the art HP-TGA to obtain high repeatability of thermogravimetric data. The obtained kinetic parameters were validated by reconstruction of the conversion (α) vs temperature (T) profiles obtained from thermogravimetric data. Lab-scale pyrolysis experiments were carried out using a setup designed in the lab to understand the effect of pressure on product yield and composition. Studying the effect of pressure on oil shale pyrolysis can help in understanding the maturation of oil shale in the subsurface retorting process.

4.1. High-pressure thermogravimetric analysis

High-pressure TGA curves are illustrated in Fig 4.1. Two distinct decomposition regions were identified from the TG-DTG curves (Fig 4.1 and 4.2) corresponding to moisture loss in the preheating zone (50°C to 200°C), and organic decomposition zone (350°C to 650°C). Moisture loss of around 5 wt% was observed in all the experiments. At high pressure, the removal of produced water vapor may also be affected by the effectiveness of the sweep gas. The mass loss corresponding to the temperature interval of organic matter decomposition ranged from 17 wt% @ 5 bar to 22wt % @ 30 bar. Under atmospheric pressure 21% organic matter mass loss was observed[151]. A marginal increase in mass loss corresponding to organic matter decomposition was observed at high pressure. During High-pressure pyrolysis, the organic matter decomposition temperature ranged from 350°C to 650°C. Previous studies conducted under atmospheric conditions showed the organic matter degradation to occur from 300°C to 600°C[151]. This may have occurred because, high pressure increases the hydrocarbon volatilization temperature and reduces the rate of vaporization of oil leading to a delay in hydrocarbon expulsion[63, 64]. Minerals such as calcite and dolomite show degradation above 600°C to 800°C. A small amount of mass loss (2 wt%) corresponding to the mineral matter and char degradation was observed in the TG-DTG plot with a shoulder occurring from 650°C to 750°C at each pyrolysis pressure.

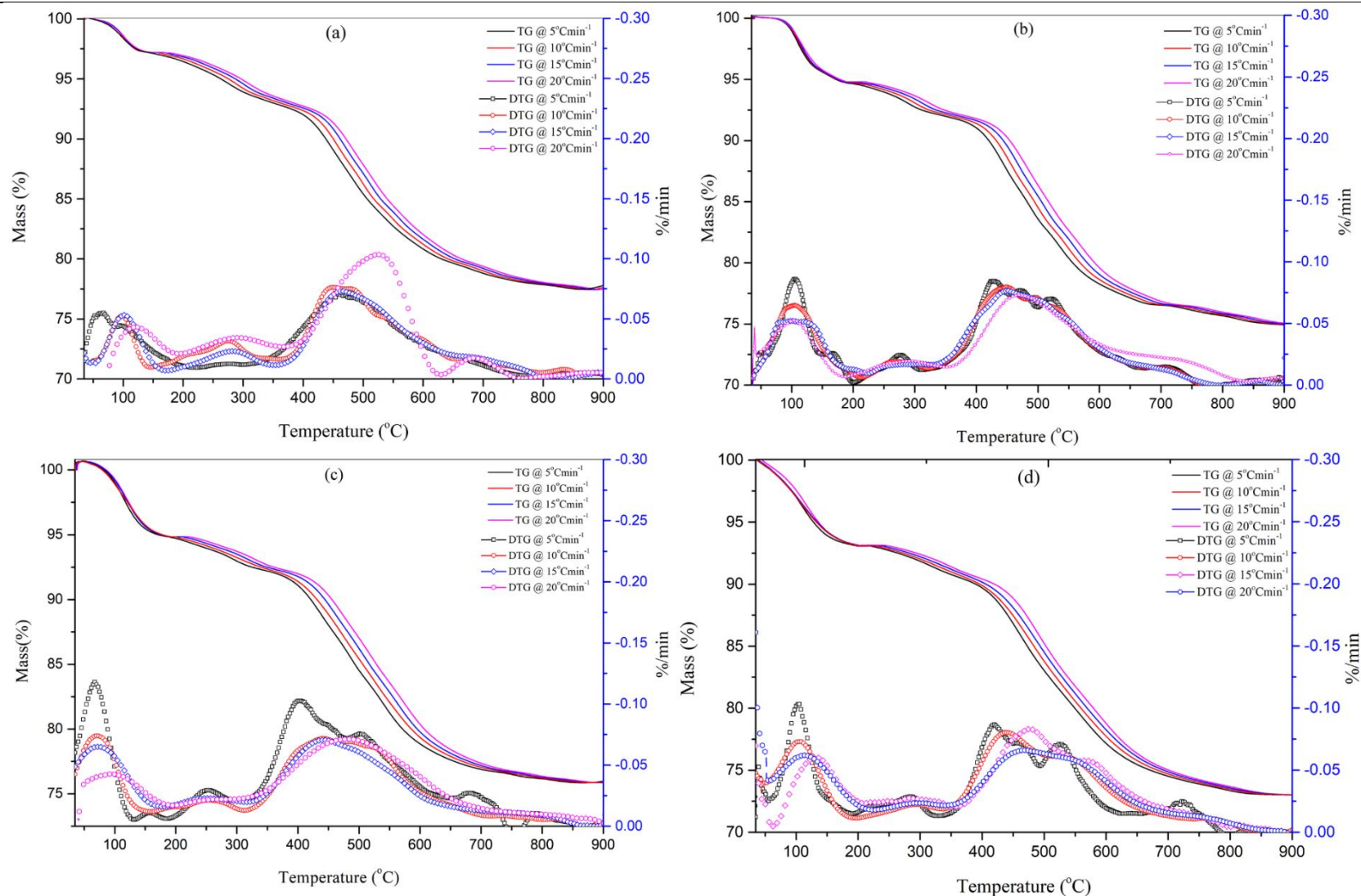


Fig 4.1. TG-DTG profiles of oil shale at 5, 10, 15 and 20°C/min for (a) 5 bar, (b) 10 bar, (c) 20 bar, and (d) 30 bar.

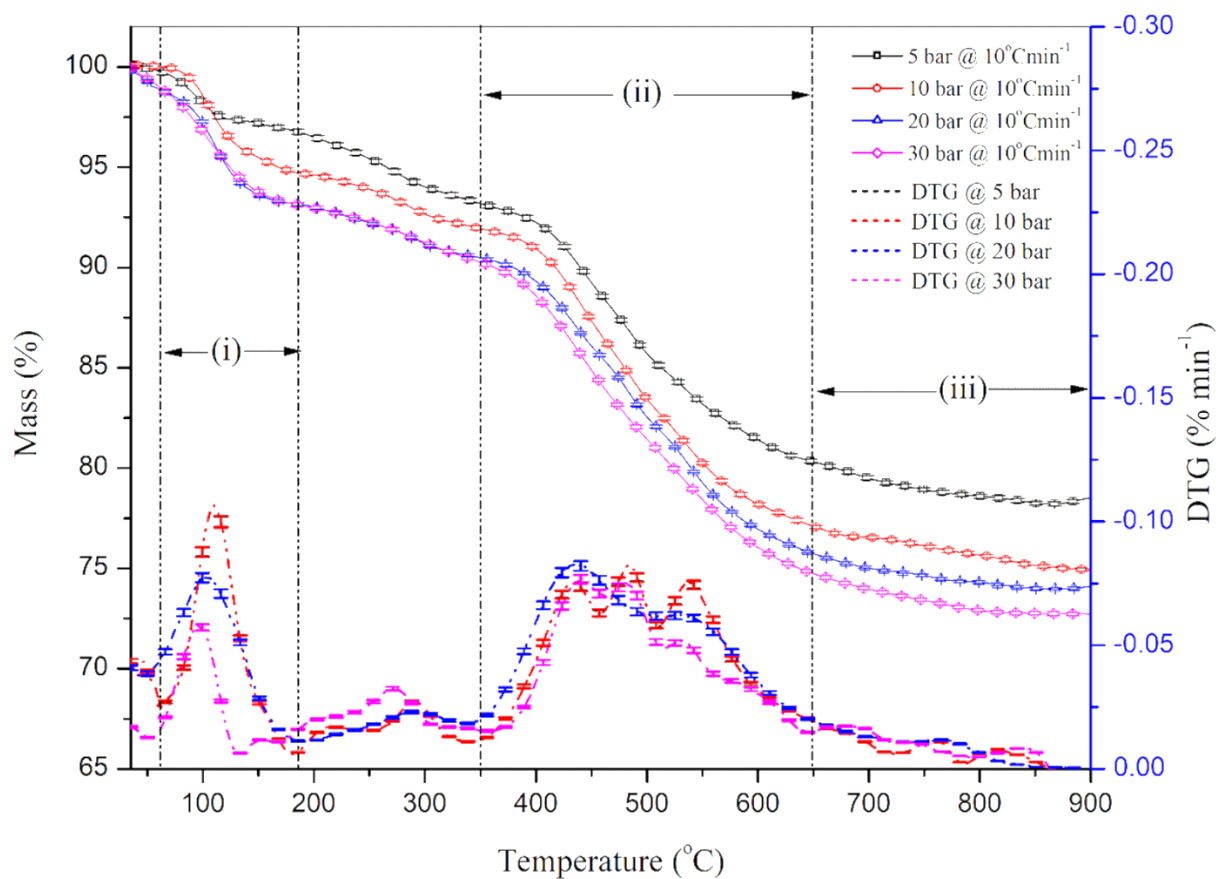


Fig 4.2. TG-DTG profiles of oil shale with error bar at 10°C/min for 5, 10, 20 and 30 bar pressure, highlighting (i) moisture loss, (ii) organic matter and (iii) mineral matter decomposition with error bar.

4.2. Kinetic study

4.2.1. Determination of apparent activation energy

The organic matter decomposition range identified from HP-TGA data (350°C to 650°C) were used for the determination of kinetic parameters. Detailed methodology of the kinetic study is presented in section 2.13 of Materials and methodology. HP-TGA data were normalized from 0 to 1 prior to the calculation of apparent activation energy values. The error in apparent activation energy values were determined by repeating the TG runs and calculating the apparent activation energy values for different number of heating rate combination (5, 10, 15, 20° C/min and 5, 10, 20° C/min) at each pyrolysis pressure, and are shown in Fig 4.3 and 4.4, respectively. The mean error in apparent activation energy values were found to be 4.6%, 1.75%, and 1.2% for Friedman, Starink, and AIC method respectively. The kinetic parameters obtained for each pressure are summarized in Table 4.1. The range of apparent activation energy values varied with pressure, with distinct patterns at each pressure. It was observed that with increase in pressure, the values of apparent activation energy values initially increased for each isoconversional method from 5 bar to 20 bar, and then decreased at 30 bar. At 5-bar pressure, Friedman method exhibited mean apparent activation energy of 600 kJmol⁻¹, Starink methods showed a mean apparent activation energy value of 535 kJmol⁻¹, and AIC method showed the least mean apparent activation energy of 434 kJmol⁻¹. At 10-bar pressure, Friedman method displayed mean apparent activation energy of 585 kJmol⁻¹, Starink method showed mean apparent activation energy value of 545 kJmol⁻¹ and AIC method showed mean apparent activation energy value of 443 kJmol⁻¹. For Friedman and Starink method, the apparent activation energy values increased from $\alpha = 0.05$ to 0.1, then decreased up to $\alpha = 0.38$ and increased at $\alpha = 0.4$, again decreased from $\alpha = 0.42$ to 0.54, and increased from $\alpha = 0.56$ to 0.64, finally decreasing from $\alpha = 0.66$ to 0.98. AIC method showed a constant distribution of apparent activation energy values considering the error percentage from $\alpha = 0.2$ to 0.7 and the

values decreased from $\alpha = 0.72$ to 0.98 . At 20-bar pressure, Friedman method showed mean apparent activation energy of 612 kJmol^{-1} , Starink method showed mean apparent activation energy of 580 kJmol^{-1} , and AIC method reported a mean apparent activation energy value of 451 kJmol^{-1} . For Friedman and Starink method the activation energies followed a decreasing trend from $\alpha = 0.05$ to 0.4 , increasing at $\alpha = 0.42$ to 0.54 , decreasing from $\alpha = 0.56$ to 0.6 , again increasing at $\alpha = 0.62$ to 0.7 and finally decreasing from, $\alpha = 0.72$ to 0.98 . However, AIC method showed apparent activation energy values to increase from 0.05 to 0.3 , constant from 0.3 to 0.5 considering the error percentage, and at later conversions follow a similar trend with Friedman and Starink method. At 30-bar pressure, Friedman method showed the highest mean apparent activation energy of 435 kJmol^{-1} , followed by Starink method with mean apparent activation energy of 368 kJmol^{-1} , and AIC method showed the least mean apparent activation energy value of 341 kJmol^{-1} . The apparent activation energy appeared to decrease from $\alpha = 0.05$ to 0.3 , increase from $\alpha = 0.32$ to 0.58 , remained constant from $\alpha = 0.6$ to 0.88 and eventually increased from $\alpha = 0.9$ to 0.95 . The mean apparent activation energy values for each pressure appeared to be higher than the apparent activation energy at atmospheric pressure[151]. The increase in activation energy values with increase in pressure was previously reported by Burnham and McConaghy[64] to occur due to the increase in hydrocarbons volatilization temperature and delay in vaporization of oil due to the manifestation of cracking because of prolonged exposure to secondary reactions. Burnham [63, 199] reported the increase in apparent activation energy value with increase in pyrolysis pressure and presented a mathematical expression showing activation energy as a function of temperature, pressure, and purge rate. The increase in activation energy due to the occurrence of secondary reactions was previously stated by Campbell et al [157]. The secondary reactions occur due to the reaction of the hydrocarbon vapors with the solid reactants and later due to the

decomposition of the char to produce hydrocarbon gases. The effect of vaporization and cracking of oil is noticeable in product yield and characterization later in the manuscript.



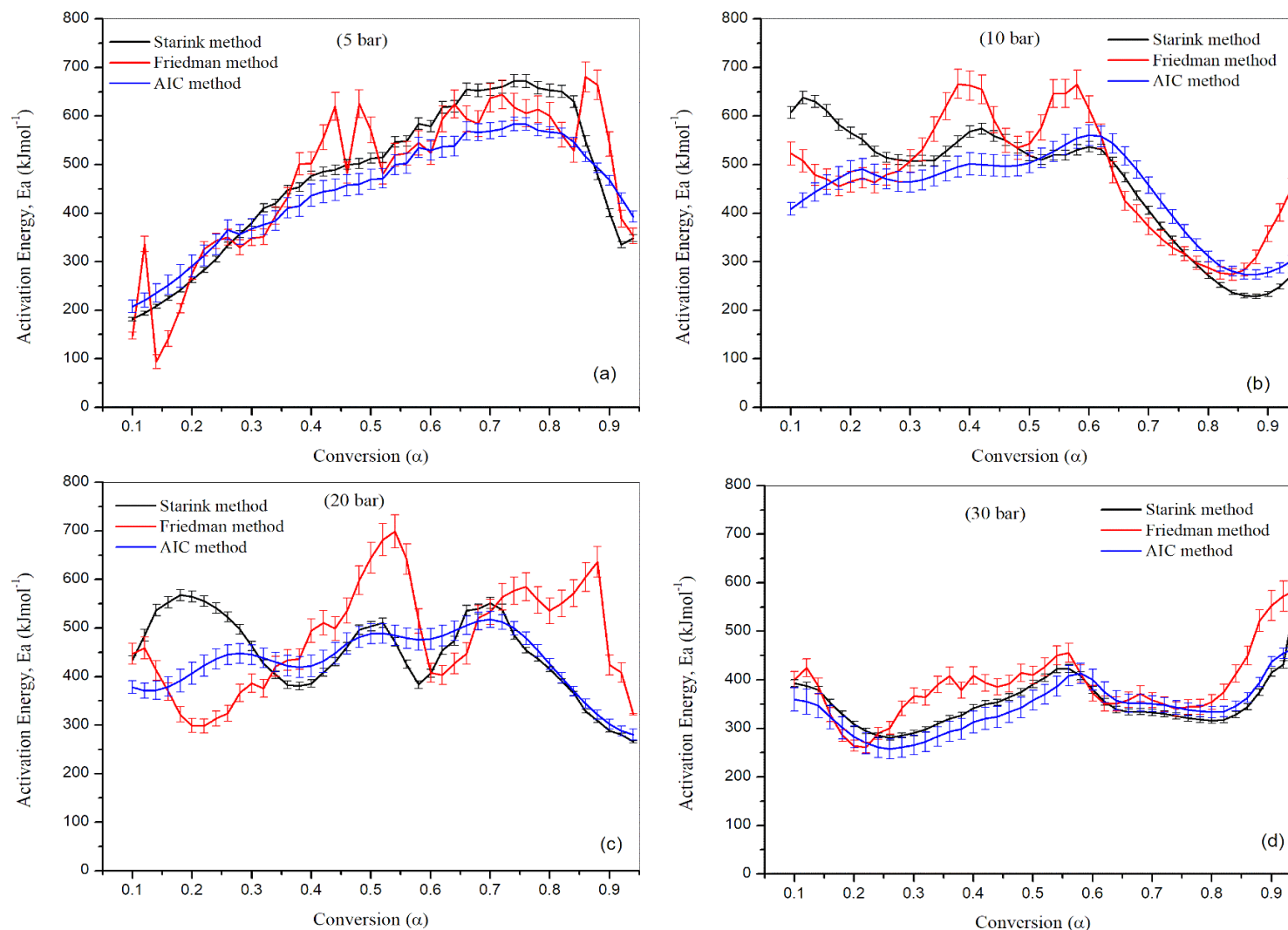


Fig 4.3. Distribution of activation energy values for different isoconversional methods at pressure values of (a) 5, (b) 10, (c) 20, and (d) 30 bar calculated using four heating rates (5, 10, 15, and $20^\circ\text{C}/\text{min}$).

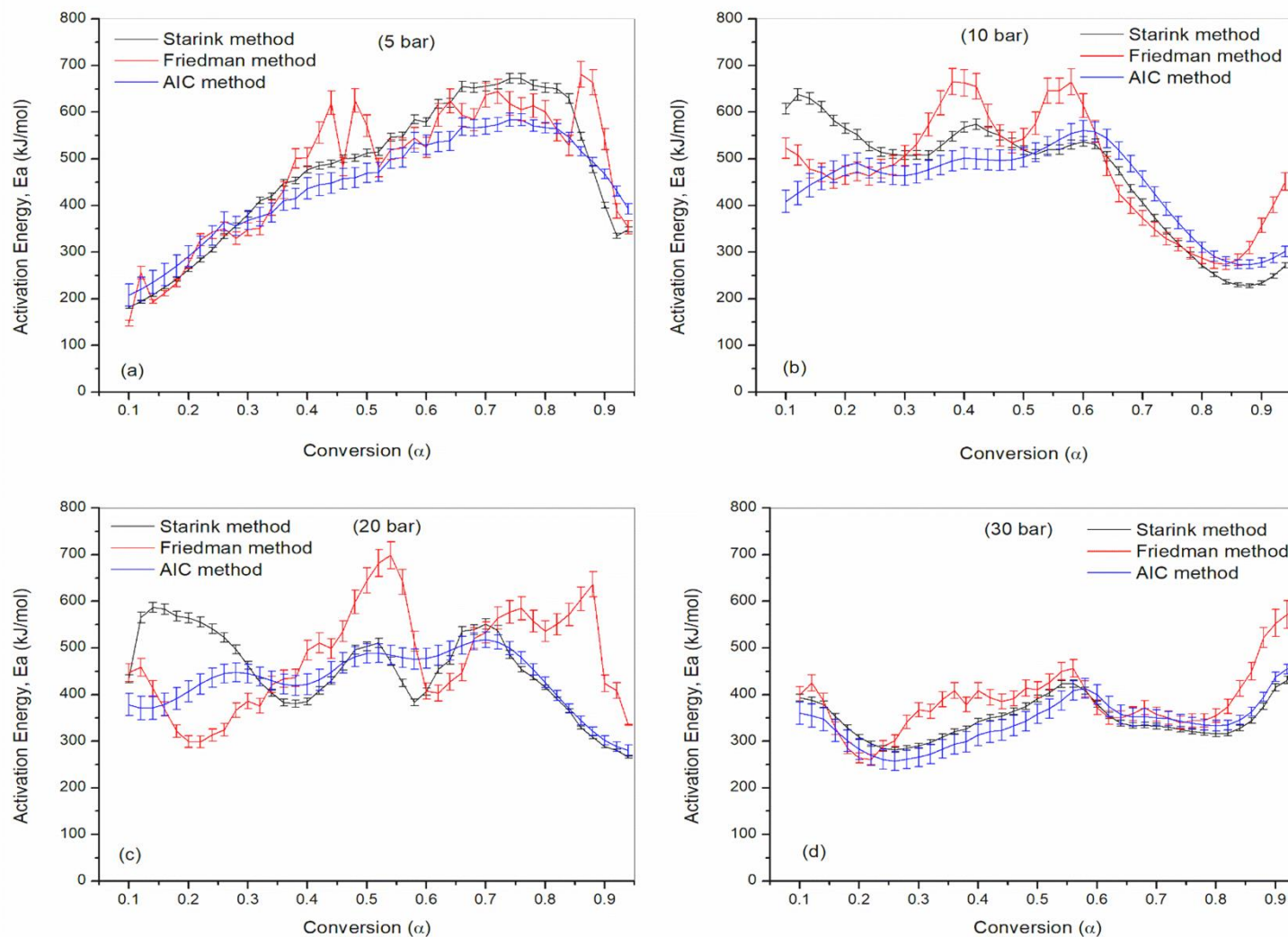


Fig 4.4. Distribution of activation energy values for different isoconversional methods at pressure values of 5, 10, 20, and 30 bar calculated using three heating rates (5, 10 and 20°C/min).

4.2.2. Determination of reaction model and pre-exponential factor

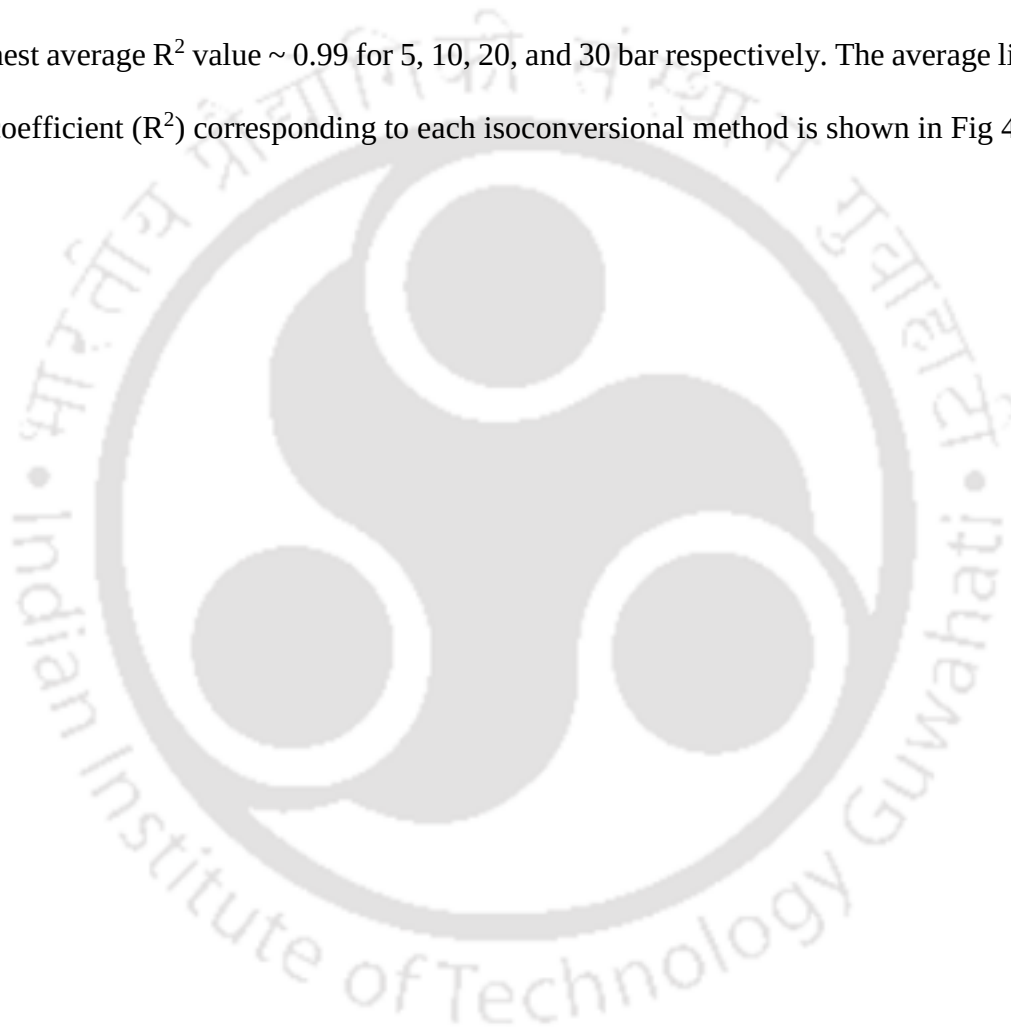
The mean derived activation energy values were used to determine the kinetic model and pre-exponential factor. The kinetic models were determined using Criado master plot [180-182]. AIC model showed highest co-relation factor (mean $R^2 = 0.98$) for experimental $f(\alpha)$ vs theoretical $f(\alpha)$. The theoretical master plots using $\left(\frac{Z(\alpha)}{Z(0.5)}\right)$ of different reaction mechanisms vs conversion, α and the experimentally determined model plots using AIC method for each pressure at heating rate of 10°C/min are illustrated in Fig 4.5(a), and the Criado plots for Friedman and Starink method are presented in Figure 4.6 (a-b). The correspondence between experimental $f(\alpha)$ and theoretical $f(\alpha)$ for AIC model are shown in Fig 4.5(b), and for Friedman and Starink model are shown in Fig 4.7(a-b). The degradation kinetics of oil shale under the influence of pressure (5, 10, 20, and 30 bar) showed oil shale pyrolysis to follow D3 diffusion, F2 second order, and A3 Avrami Eroffev reaction models. Our previous studies [151] on oil shale kinetics at ambient pressure also reported the occurrence of multiple reaction models as the decomposition progress. The changes in the reaction models during the degradation process indicates the production of smaller hydrocarbon compounds from the reactions on the surface of the organic matter and diffusion through the pores to the surface due to heat transfer gradient (D3 diffusion). At higher conversion, the governing reactions appeared to be F2 and A3 nucleation models. The range of the models varied throughout the conversion (α) with increase in pressure. At 5-bar and 10 bar pressure, D3 diffusion model appeared from $\alpha = 0.02$ to 0.5, and shifted to second-order reaction model at $\alpha = 0.5$ to 0.88, and A3 Avrami Eroffev from $\alpha = 0.90$ to 0.95. At 20-bar pressure, D3 diffusion occurred up to $\alpha = 0.4$, and followed second-order diffusion from $\alpha = 0.42$ to 0.74. From $\alpha = 0.76$ the reaction model shifted towards A3 Avrami Eroffev up to $\alpha = 0.95$. At 30-bar pressure, D3 diffusion model appeared up to $\alpha = 0.38$. Second-order reaction model ranged from $\alpha = 0.40$ to 0.60 and shifted to A3 Avrami Eroffev from $\alpha = 0.62$ to 0.95 (Table 4.1). Previous kinetic studies on oil shale at atmospheric

pressure showed the occurrence of D3 diffusion followed by A2 Avrami Eroffev model [151]. D3 diffusion model may occur due to the production of smaller hydrocarbon compounds from the reaction on the surface of the organic matter and diffusion from pores in the mineral matrix as influenced by heat transfer during pyrolysis. It appeared as the initial step of oil shale degradation during high pressure as well as atmospheric pyrolysis[151]. At high pressure, the hydrocarbon volatilization temperature increases and it reduces the rate of vaporization. This leads to delays in the release of produced hydrocarbons and the occurrence of cracking and secondary reactions[35, 63]. The A3 Avrami Eroffev reaction model being a nucleation model may have occurred as a result of coking reaction leading to the formation of char [199, 206]. The comparison of experimental $f(\alpha)$ vs theoretical $f(\alpha)$ presented in Fig 4.5(b) verifies the reaction models identified from the Criado master plot. It may be noted that the experimental $f(\alpha)$ curves in Fig 4.5(b) followed a similar path to the experimental $f(\alpha)$ vs theoretical $f(\alpha)$ plot reported by Burnham[51], who reported the reaction models for coal and petroleum source rocks to follow a distributed reactivity model.

The pre-exponential factor was calculated by substituting the apparent activation energies into a linear logarithmic Arrhenius kinetic equation, which was then used to calculate $Af(\alpha)$ for each conversion point. From $Af(\alpha)$ the pre-exponential factor was determined by considering the determined reaction models $f(\alpha)$ from the Criado master plot. The values of the pre-exponential factor determined for each conversion range corresponding to the determined reaction models are presented in Table 4.1. Subsequently, the values of $\ln(A)$ were plotted against E_a obtained by AIC method for each operating pressure in Fig 4.8(a-d). These constable plots showed the extent of occurrence of identified reaction models (D3, F2, and A3) throughout the entire organic degradation period, with an average linearity coefficient.

4.2.3. Re-construction of thermogravimetric data

The kinetic triplets obtained from different methods were used for reconstruction of the conversion vs temperature profiles (α vs T). The simulated vs experimental data plots for each isoconversional method at 10 bar for each heating rate (5, 10, 15, and 20°C/min) are shown in Fig 4.9. Comparison of regression analysis of average linearity fitting coefficient (R^2) corresponding to each isoconversional method at each pressure showed AIC method to exhibit the highest average R^2 value ~ 0.99 for 5, 10, 20, and 30 bar respectively. The average linearity fitting coefficient (R^2) corresponding to each isoconversional method is shown in Fig 4.10.



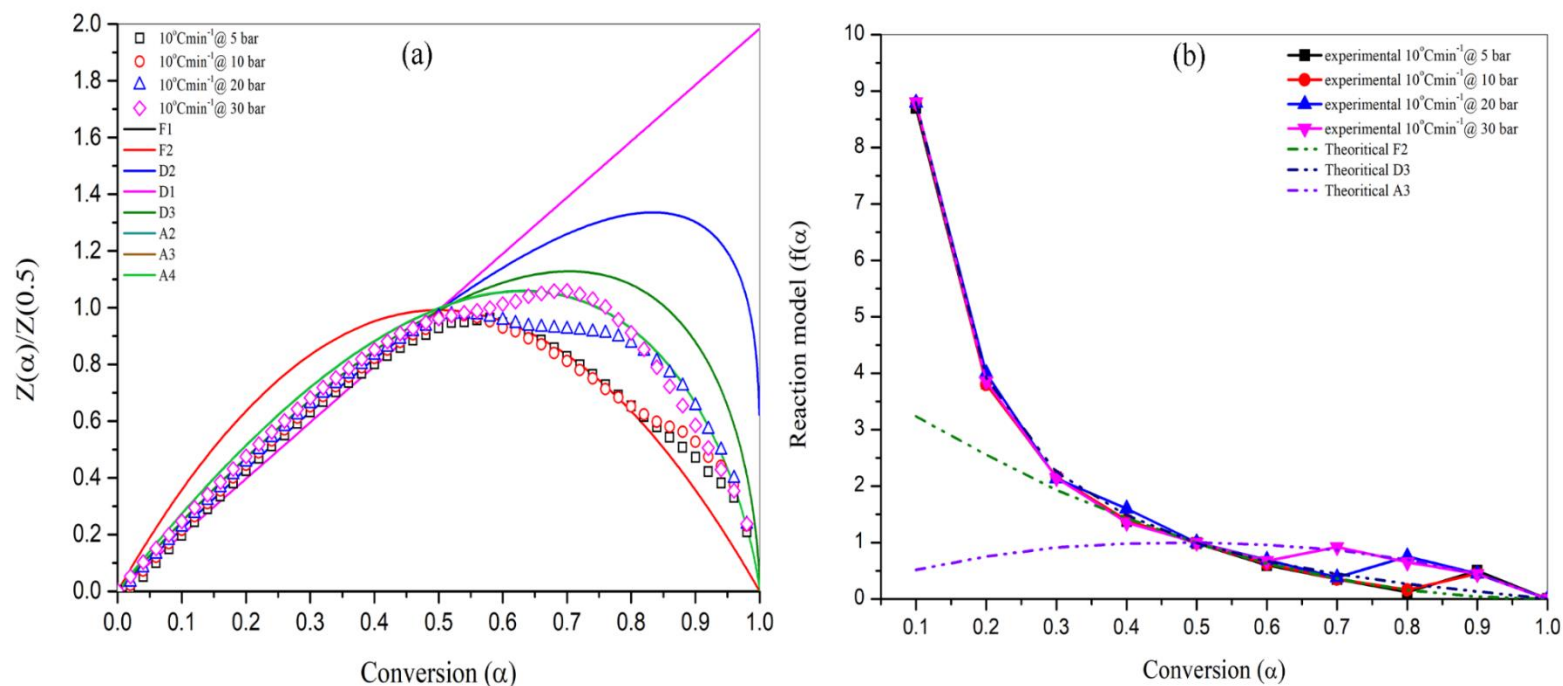


Fig 4.5. (a) Theoretical master plots of different reaction models and experimental reduced rate plots at 10°Cmin^{-1} for 5, 10, 20, and 30 bar, and (b) Experimental $f(\alpha)$ vs theoretical $f(\alpha)$ for AIC method at 10°Cmin^{-1} for 5, 10, 20 and 30 bar pressure.

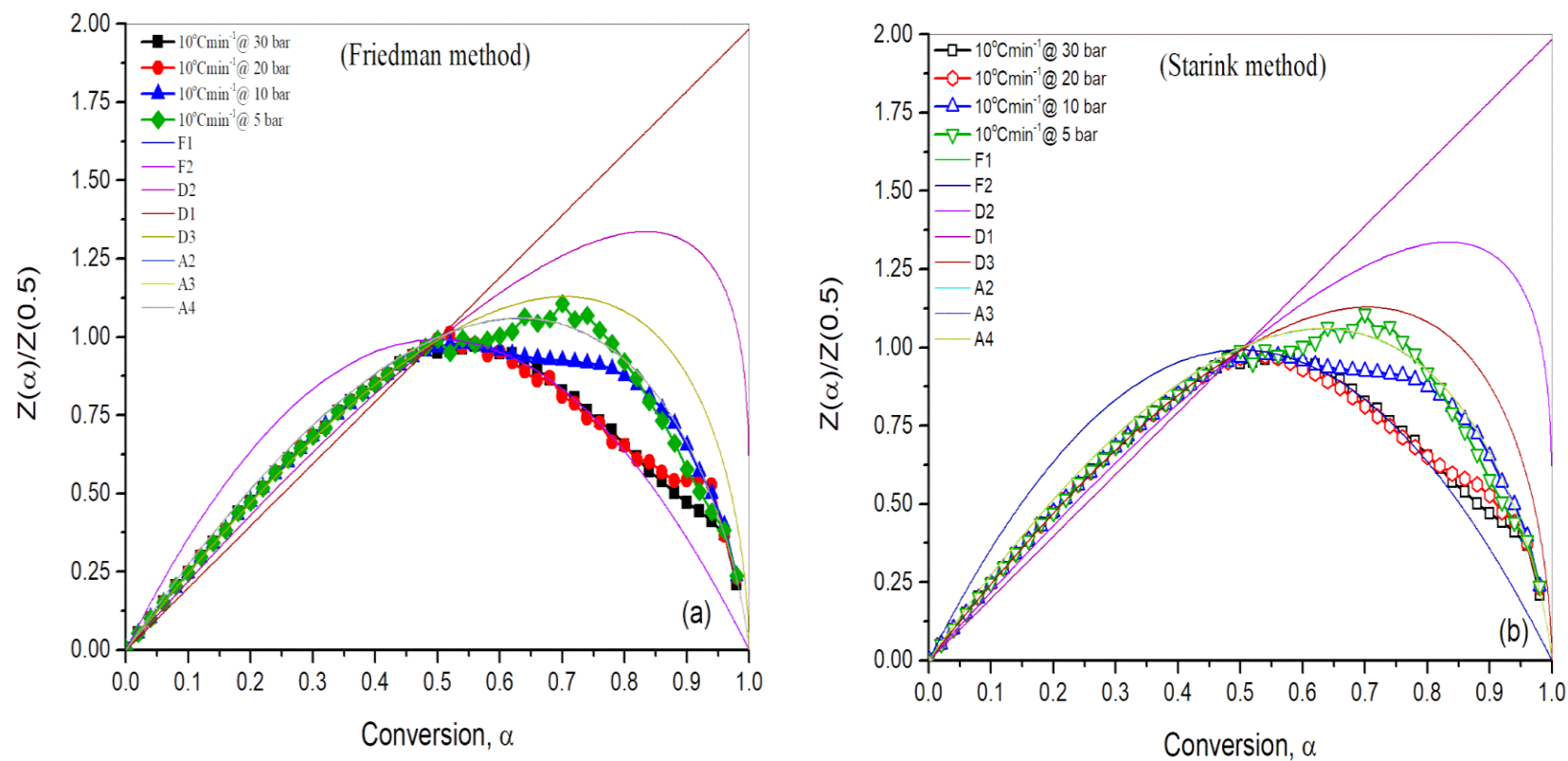


Fig 4.6. Criado master plot using (a) Friedman (b) Starink method at 10°Cmin^{-1} for 5, 10, 20 and 30 bar pressure.

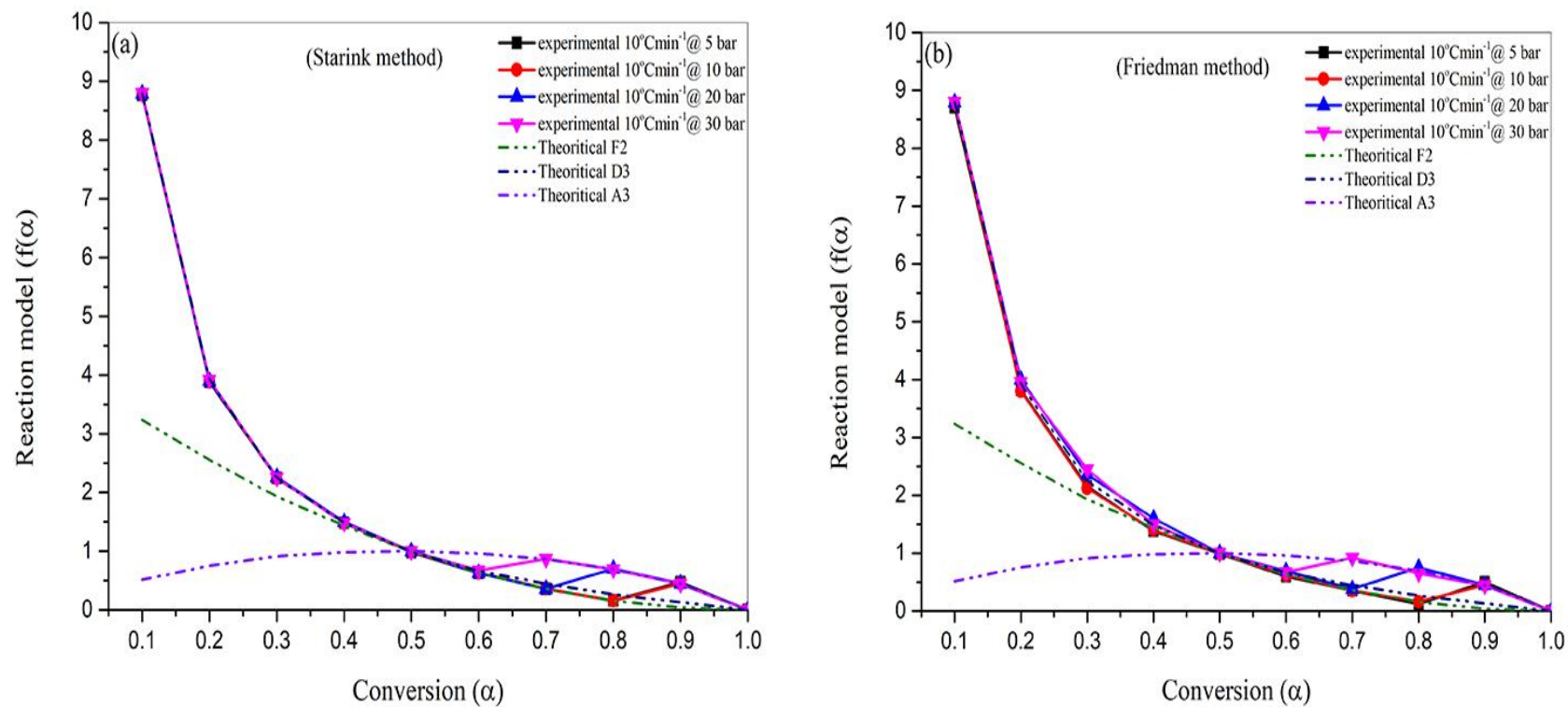


Fig 4.7. Experimental $f(\alpha)$ vs theoretical $f(\alpha)$ for (a) Starink, and (b) Friedman method at $10^{\circ}\text{Cmin}^{-1}$ for 5, 10, 20 and 30 bar pressure.

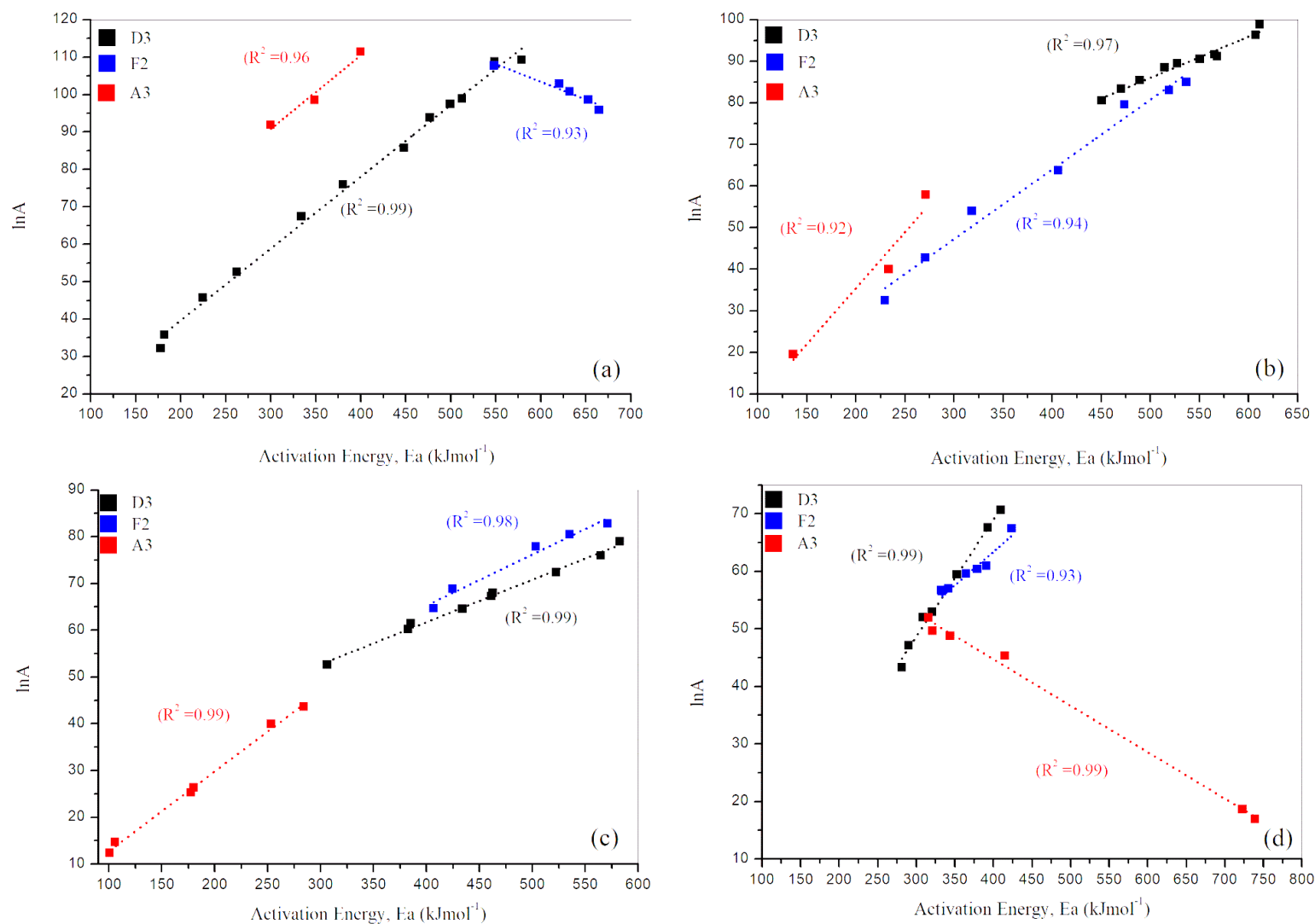


Fig 4.8. Constable plots for AIC method at (a) 5 bar, (b) 10 bar, (c) 20 bar and (d) 30 bar.

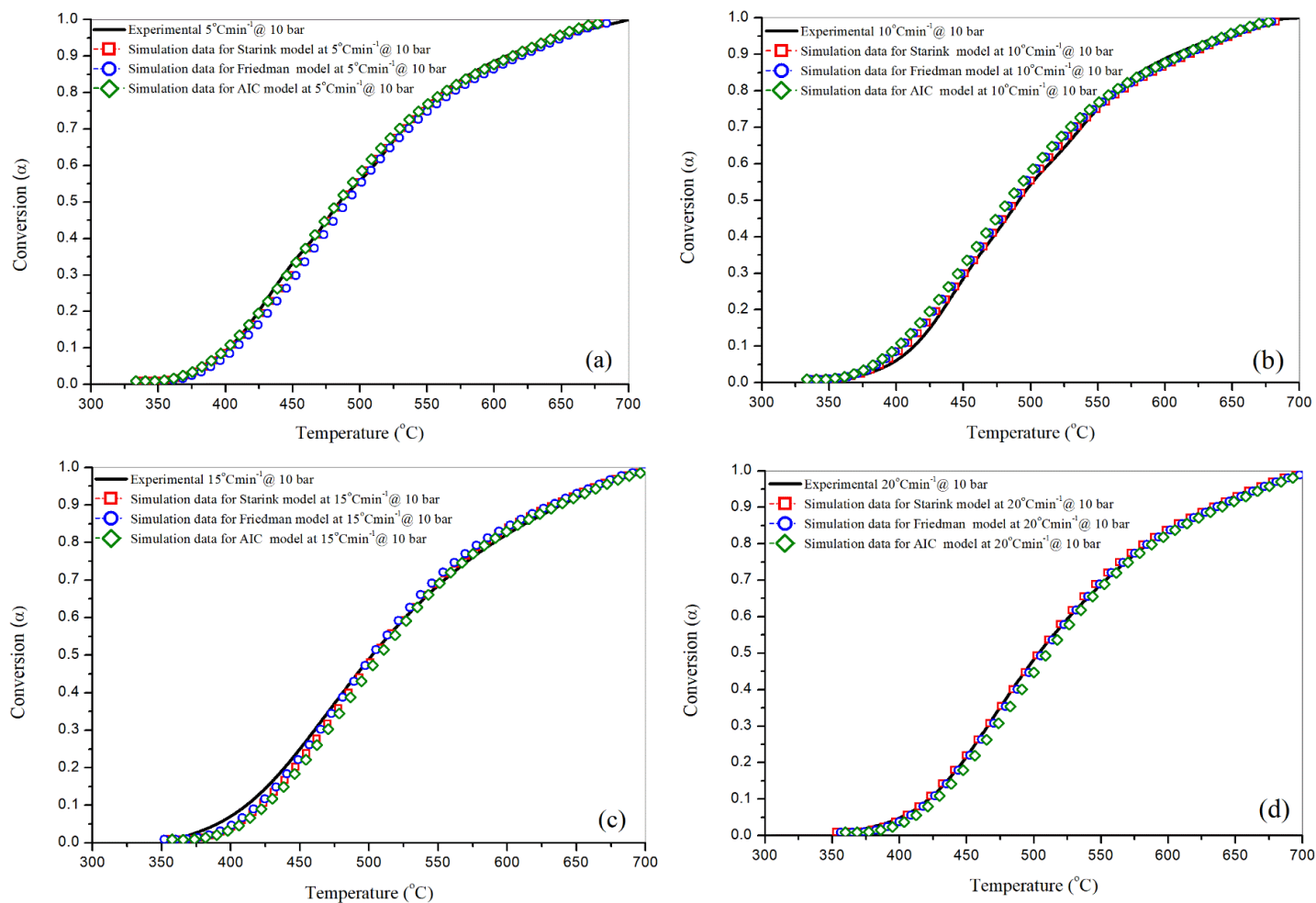


Fig 4.9. Fitness of simulated to experimental TG data for AIC, Friedman and Starink method at 10 bar pressure at heating rate of (a) 5°C/min, (b) 10°C/min, (c) 15°C/min, and (d) 20°C/min.

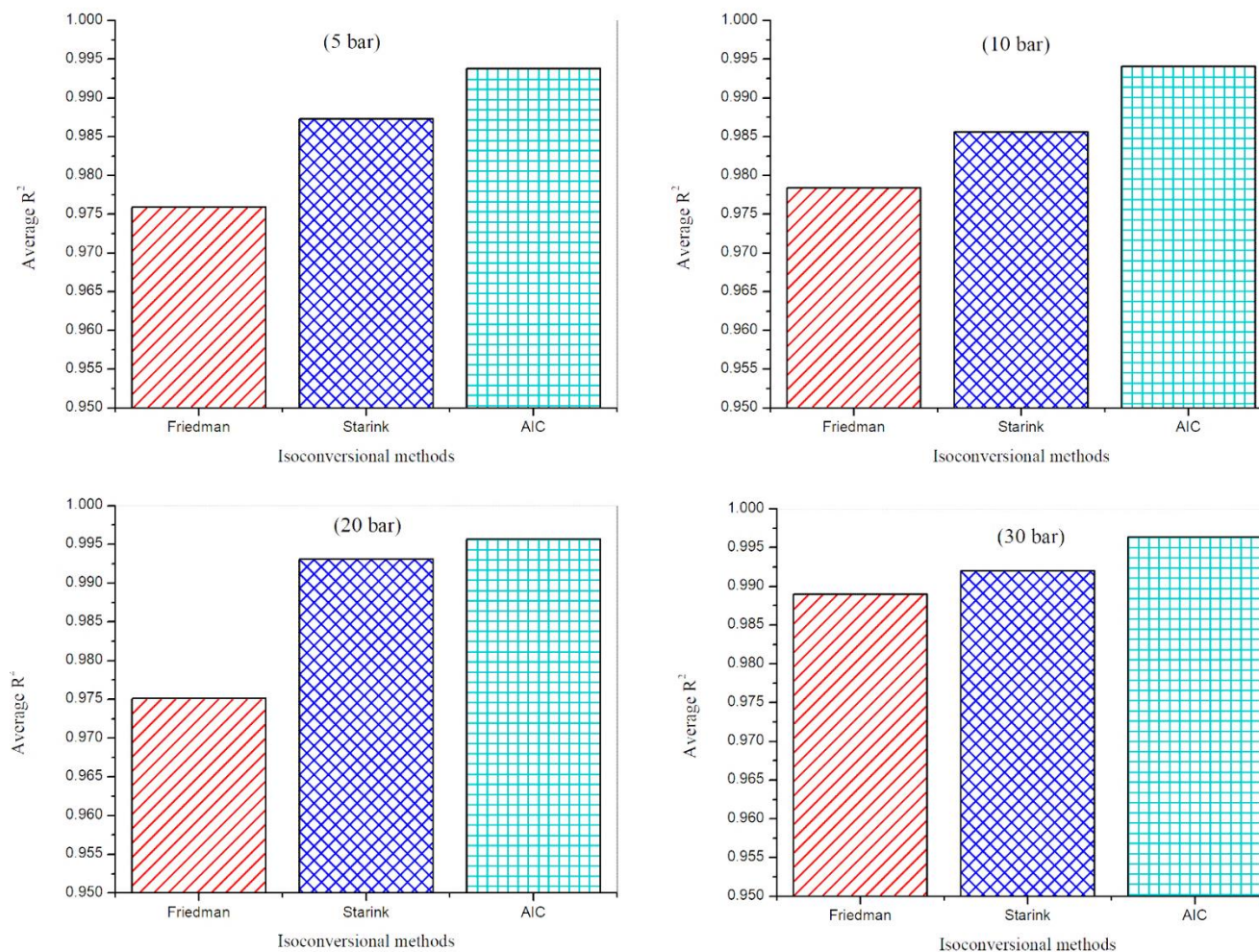


Fig 4.10. Comparison of different isoconversional methods based on linear average coefficient (average R^2) value between experimental and reconstruction and experimental α vs T profiles at (a) 5 bar, (b) 10 bar, (c) 20 bar and (d) 30 bar pyrolysis pressure.

Table 4.1. Kinetic parameters obtained using isoconversional techniques.

Pressure (bar)	Isoconversional techniques	Activation energy, Ea (kJ/mol)	Pre-exponential factor, A(sec ⁻¹)	Reaction model, f(α)
5	Friedman method	144-631	1.03×10^{12} - 2.36×10^{48}	D3 ($\alpha = 0.05$ to 0.5), F2 ($\alpha = 0.5$ to 0.88) and
	Starink method	180-670	1.91×10^{12} - 1.30×10^{48}	A3 ($\alpha = 0.90$ to 0.95)
	AIC method	207-581	1.75×10^{12} - 2.13×10^{48}	
10	Friedman method	273-661	1.07×10^{16} - 6.63×10^{43}	D3 ($\alpha = 0.05$ to 0.5),
	Starink method	287-646	2.06×10^{15} - 3.99×10^{42}	F2 ($\alpha = 0.5$ to 0.88) and
	AIC method	300-567	2×10^{15} - 4.11×10^{42}	A3 ($\alpha = 0.90$ to 0.95)
20	Friedman method	250-674	2.24×10^6 - 1.83×10^{33}	D3 ($\alpha = 0.05$ to 0.40),
	Starink method	284-618	1.69×10^9 - 1.01×10^{33}	F2 ($\alpha = 0.42$ to 0.74) and
	AIC method	274-505	1.62×10^9 - 1.55×10^{33}	A3 ($\alpha = 0.76$ to 0.95)
30	Friedman method	263-605	2.36×10^{20} - 2.24×10^{29}	D3 ($\alpha = 0.05$ to 0.38),
	Starink method	400-604	1.76×10^{20} - 1.94×10^{29}	F2 ($\alpha = 0.40$ to 0.60) and
	AIC method	259-457	3.95×10^{20} - 2.05×10^{30}	A3 $\alpha = (0.62$ to $0.95)$

4.3. Lab-scale pyrolysis

The yields of the products, oil, gas, char, and aqueous phase from the High-pressure pyrolysis of the samples with standard deviation are summarized in Table 4.2 and Fig 4.11(a-d). A significant variation was found in the product yield with a change in heating rate. At higher heating rates ($10\text{ }^{\circ}\text{Cmin}^{-1}$ and $20^{\circ}\text{Cmin}^{-1}$) the oil yield decreased drastically and no significant oil could be collected for analysis. The decrease in oil yield with increase in heating rate and pressure has previously been reported by Corredor and Deo[68] and Salhi et al.[215] The percentage of spent shale was observed to be identical for each heating rate which showed that the decomposition products were in condensable form. At 5 bar, with increase in pyrolysis temperature from 450°C to 650°C the oil yield increased to 600°C and decreased while approaching 650°C . At pyrolysis pressure of 10, 20, and 30 bar, the oil yield increased to 550°C and then remained constant within the error limits. While the gas yield increased linearly with increase in pyrolysis temperature except at 5 bar pyrolysis pressure when the gas yield increased to 550°C and remained constant to 600°C and further increased at 650°C (Fig. 4.12). A minute amount of aqueous phase in the range of (0.6 to 1.5 (wt/wt%)) was observed and separated from the obtained oil by gravity separation. Maximum oil yields and relatively small gas yields were obtained when heating at $5\text{ }^{\circ}\text{Cmin}^{-1}$ to $600\text{ }^{\circ}\text{C}$ for all operating pressures, and this condition was considered to be the optimum condition. Therefore, products obtained at this condition were subjected for characterization. The maximum oil yields at 5 bar, 10 bar, 20 bar and 30 bar were obtained as 11.5% ($\rho = 879\text{ g/cm}^3$), 11.09% oil ($\rho = 868\text{ g/cm}^3$), 10.09% ($\rho = 841\text{ g/cm}^3$) and 10.02% ($\rho = 839\text{ g/cm}^3$) respectively. The maximum oil yield obtained at each pressure was observed to be lower compared to oil obtained during pyrolysis at atmospheric pressure (14.5%)[22]. This phenomenon was previously stated by Burnham[63] to occur due to the higher residence time of oil in the reactor leading to coking and cracking reactions. The decrease in molecular weight and increase in vapor pressure of the oil is directly affected by

the increase of residence time, which is also reflected in the density of the collected oil. The decrease in the density of oil with increase in pressure and the increase in the percentage of gaseous products formed with increase in pyrolysis temperature indicated the cracking of hydrocarbons for the formation of lighter compounds. Similar findings have been previously reported by various researchers showing the occurrence of lower boiling point compounds in the pyrolytic oils obtained at high pressure[63, 64, 68, 216]. This could be the reason for the occurrence of high activation energy values and also the occurrence of the nucleation mechanism (A3) related to cracking and coking reaction in the current study.

Table 4.2. Pyrolysis yield at different pressure and pyrolysis temperature at heating rate of 5°C/min.

Pressure	Temperature (°C)	Spent shale (wt/wt) (%)	Oil yield (wt/wt) (%)	Gas yield (wt/wt) (%)	Aqueous phase (wt/wt) (%)
5	650	81±1.2	7.5±0.6	11.5±0.5	0.7±0.5
	600	77.5±2.0	11.5±2.0	9.5±1.9	1±0.3
	550	80±2.4	9.9±2.1	11±2.0	1.1±0.7
	500	87±3.7	5.9±1.0	5±0.8	1.3±0.4
	450	92.3±5.6	1.3±2.1	4.4±3.0	1.5±0.5
10	650	74.2±2.1	8.8±1.0	15.9±1.1	0.6±0.2
	600	71.2±3.0	11.1±3.0	13.9±3.1	1.0±0.2
	550	78.5±1.8	8.4±1.7	10.2±1.9	1.2±0.1
	500	84.2±2.9	6.4±0.7	7.2±1.0	1.4±0.2
	450	91.3±4.0	1.5±1.3	5.1±1.8	1.5±0.5
20	650	72.4±2.1	8.9±0.9	17.5±0.8	0.6±0.4
	600	70.7±1.7	10.9±1.8	15.5±1.5	1.0±0.2
	550	76.8±3.2	7.5±2.0	9.5±2.0	1.1±0.3
	500	82.9±2.0	6.5±0.7	8.5±1.5	1.3±0.5
	450	92.3±4.7	1.6±2.6	4±2.0	1.5±0.1
30	650	71.5±2.8	9.5±1.8	18.4±1.0	0.6±0.5
	600	71.3±2.5	10±2.0	17.4±2.5	1±0.2
	550	74.4±1.9	8.9±1.6	8.3±1.7	1.1±0.3
	500	80.6±2.9	6.9±1.3	10.3±1.7	1.3±0.4
	450	91±3.2	1.9±1.5	5±1.7	1.4±0.0

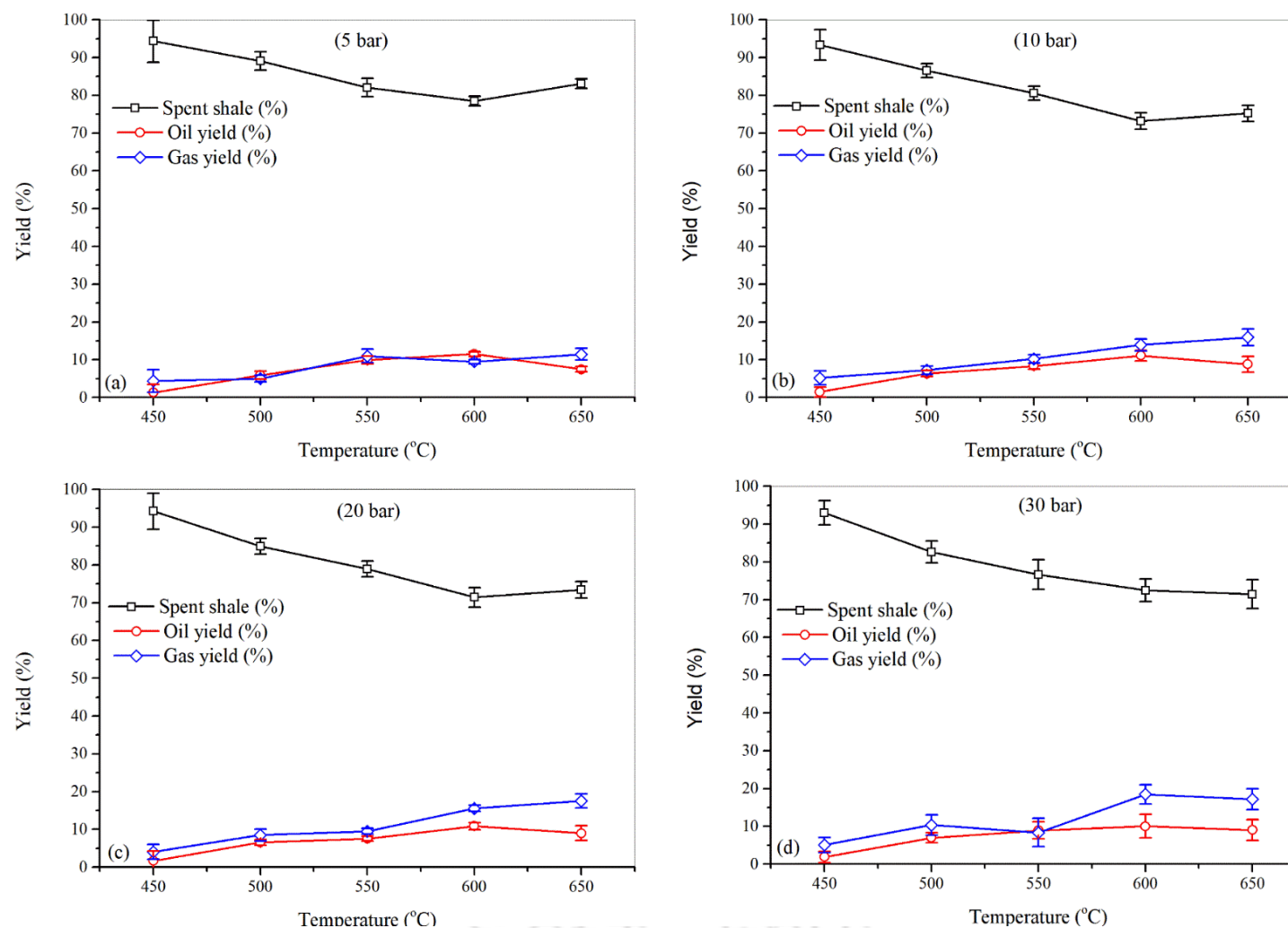


Fig 4.11. Cumulative mass loss and yield of oil, gas and spent shale at pyrolysis pressure of (a) 5 bar, (b) 10 bar, (c) 20 bar and (c) 30 bar, at heating rate of 5°C/min obtained at different pyrolysis temperature (450°C to 650°C).

4.4. Characterization of products

4.4.1. Gas chromatography (GC) analysis of pyrolytic gas

Gas chromatography (GC) analysis was performed on the gas samples collected during pyrolysis. The relative percentage of produced gases with error percentage is shown in Fig 4.12 (a-e). The mean relative concentration of identified gases obtained at pyrolysis pressure of 1 to 30 bar is tabulated in Table 4.3. At high pressure, the percentage of CH_4 and C_2 gases increased with increase in temperature. Similar observations were previously reported by Solomon et al.[217] for pyrolysis of Israeli oil shale at atmospheric pressure, who observed the increase in the concentration of CH_4 and C_2H_4 gases up to 600°C . At 5 bar pressure, the relative concentration of hydrogen increased from 350°C to 450°C and decreased from 450 to 650°C . At 10 bar pressure, the concentration increased from 350°C to 600°C and decreased at 650°C . At 20 and 30 bar pressure, the relative concentration of hydrogen decreased from 350°C to 650°C . For each pyrolysis pressure (5 – 30 bar) concentration of CO_2 decreased from 350°C to 600°C and increased sharply at 650°C . The increase in the relative percentage of CO_2 may have occurred due to the breakdown of carbonyl compounds and pyrolysis of the char at 650°C . A small concentration of CO was detected at 5 and 10 bar, from 350 to 550°C , and disappeared at higher pressure of 20 and 30 bar. From 5 to 20 bar the concentration of C_2H_2 increased with increase in temperature from 350°C to 600°C and decreased at 650°C . At 30 bar pressure, the maximum concentration of C_2H_2 was observed at 350°C . C_2H_4 gases showed a decreasing trend with increase in temperature for each pyrolysis pressure. The peak concentration of C_2H_6 occurred at 600°C at each pressure. Similarly, C_3 hydrocarbon gases (C_3H_6 and C_3H_8) increased from 350 to 600°C and decreased at 650°C . C_4H_8 (iso) showed a relatively constant concentration from 350 to 650°C at 5 and 10 bar. At 20 bar its concentration increased at 650°C and was not detected at 30 bar. At 5 bar C_4H_8 (n) showed increase with increase in temperature from 350 to 600°C and decreased at 650°C . At 10 bar, it showed a relatively constant

concentration from 350 to 650°C. Under 20 bar pressure, the concentration of C_4H_8 (n) increased from 350 to 450°C and decreased from 550 to 650°C. At 30 bar, C_4H_8 (n) showed a decreasing trend from 350 to 650°C. C_4H_{10} (iso) showed maximum concentration at 600°C for 5 and 10 bar and at 450°C for 20 and 30 bar. C_4H_{10} (n) showed maximum concentrations at 600°C from 5 to 30 bar. At pyrolysis pressure of 5 and 10 bar, C_2 and C_3 gases showed higher relative concentration from 350°C to 600°C. A similar trend was observed for CH_4 and C_4 gases collected at pyrolysis pressure of 20 and 30 bar. The increase in the relative concentration of hydrocarbon gases with pyrolysis pressure was previously reported by Burnham and McConaghy[64]. They reported that at high pressure, the pyrolytic gases peaked at 400°C (11 bar) and 430°C (53 bar), and the relative molar concentrations of C_1 to C_4 gases doubled with increase in pressure from 11 bar to 53 bar. Under atmospheric pressure, the generation of H_2 increased from 350 to 600°C and decreased at 650°C. The production of CO and CO_2 showed similar trend to that of H_2 . At 5 and 10 bar, methane showed a sharp increase with increase in temperature from 350°C to 600°C and decreased at 650°C. At 20 bar and 30 bar, the concentration of methane (CH_4) increased from 350°C up to 650°C. The increase in the concentration of methane was suggested by Burnham and McConaghy[64] to be a result of in-situ hydrogenation at high pressure. At atmospheric pressure, the concentration of C_2 hydrocarbon gases decreased from 350°C to 650°C. C_3 , C_4 , and C_5 gases increased from 350 to 550°C and decreased from 600 to 650°C. Burnham and McConaghy[64] reported the occurrence of gases at atmospheric pressure to peak around 380°C. It was observed that the relative concentrations of hydrocarbon gases (C_2 to C_4) obtained at high pressure were higher compared to the hydrocarbon gases (C_2 to C_4) obtained at atmospheric pressure at each temperature. At pressure of 5, 10, 20, and 30 bar the maximum relative concentrations of C_2 to C_4 gases were recorded to be in the range of 42 to 5.8 vol/vol%, compared to 10.8 to 3.2 vol/vol% obtained at atmospheric pressure. Other gaseous compounds such as ammonia,

hydrogen sulfide, and carbonyl sulfide may be present in the pyrolytic gases, but due to technical limitations of the TCD and FID detectors used in this study, such gases were not identified.



Table 4.3. Mean relative concentration (vol/vol %) of permanent and hydrocarbon gases collected at different temperatures during pyrolysis at 1, 5, 10, 20 and 30 bar and heating rate of 5°C/min.

Pressure (bar)	Temperature (°C)	H ₂ (%)	CH ₄ (%)	CO (%)	CO ₂ (%)	C ₂ H ₂ (%)	C ₂ H ₄ (%)	C ₂ H ₆ (%)	C ₃ H ₆ (%)	C ₃ H ₈ (%)	C ₄ H ₈ (iso) (%)	C ₄ H ₈ (n) (%)	C ₄ H ₁₀ (iso) (%)	C ₄ H ₁₀ (n) (%)	C ₅ H ₁₀ (iso) (%)	C ₅ H ₁₀ (n) (%)	C ₅ H ₁₂ (iso) (%)	C ₅ H ₁₂ (n) (%)
1	300	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	350	2.29	29.72	0.14	21.42	10.84	5.54	5.96	5.43	0.85	3.81	1.22	2.07	0.77	0.97	0.95	0.00	0.00
	450	3.44	28.69	0.03	19.61	8.55	3.48	5.76	7.71	5.82	3.46	1.74	1.81	5.25	1.09	0.82	0.28	0.38
	550	5.05	23.40	0.14	28.36	9.03	3.60	6.53	4.97	6.49	3.70	3.43	1.82	2.87	0.49	0.51	0.19	0.27
	600	6.27	45.23	0.40	22.51	10.24	3.01	3.99	1.55	0.62	1.36	0.08	4.74	0.00	0.00	0.00	0.00	0.00
	650	0.46	70.42	1.90	24.26	0.00	0.00	3.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	300	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	350	0.90	2.41	0.53	36.58	17.95	27.53	6.64	0.38	4.98	1.81	0.30	0.00	0.00	0.00	0.00	0.00	0.00
	450	10.15	4.10	0.05	26.10	23.54	26.67	5.13	0.56	1.03	2.41	0.26	0.00	0.00	0.00	0.00	0.00	0.00
	550	2.08	22.45	0.29	18.43	32.70	7.33	7.16	4.85	0.57	1.88	0.51	0.51	1.23	0.00	0.00	0.00	0.00
	600	0.18	20.66	0.00	11.42	41.99	12.35	5.85	2.64	0.47	1.60	0.65	0.65	1.55	0.00	0.00	0.00	0.00
	650	0.45	8.47	0.00	55.07	26.32	4.84	0.61	1.06	0.91	0.45	0.30	0.30	1.21	0.00	0.00	0.00	0.00
10	300	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	350	0.65	1.83	0.47	27.01	27.01	31.44	5.26	0.30	4.02	1.83	0.18	0.00	0.00	0.00	0.00	0.00	0.00
	450	1.09	2.33	0.74	32.44	29.42	19.86	4.95	0.45	4.36	2.43	0.25	0.40	1.29	0.00	0.00	0.00	0.00
	550	1.21	29.01	0.00	16.04	24.33	16.38	6.64	2.58	0.46	1.68	0.44	0.52	0.70	0.00	0.00	0.00	0.00
	600	1.75	29.65	0.00	9.43	31.69	13.47	7.61	2.17	0.44	1.48	0.37	0.54	1.40	0.00	0.00	0.00	0.00
	650	1.05	18.32	0.00	55.79	16.00	0.21	1.89	1.47	1.26	2.11	0.42	0.21	1.26	0.00	0.00	0.00	0.00

20	300	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	350	0.27	4.13	0.00	17.37	29.28	28.95	5.25	2.36	1.82	1.50	9.06	0.00	0.00	0.00	0.00	0.00	0.00
	450	0.24	9.16	0.00	16.93	19.63	3.63	6.08	2.25	1.90	2.21	11.99	23.53	2.45	0.00	0.00	0.00	0.00
	550	0.08	35.91	0.00	13.17	12.76	2.53	4.25	1.61	1.06	1.35	9.94	15.53	1.82	0.00	0.00	0.00	0.00
	600	0.00	33.65	0.00	4.85	26.28	2.52	4.96	1.41	0.98	1.05	8.63	13.76	1.92	0.00	0.00	0.00	0.00
	650	0.00	50.29	0.00	31.55	2.44	1.05	0.47	0.70	0.47	6.87	4.77	0.47	0.93	0.00	0.00	0.00	0.00
30	300	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	350	0.23	4.15	0.00	16.84	29.71	20.15	4.52	2.99	2.29	2.10	17.02	0.00	0.00	0.00	0.00	0.00	0.00
	450	0.12	8.92	0.00	12.19	20.40	5.73	8.00	2.70	2.08	2.36	13.94	21.42	2.14	0.00	0.00	0.00	0.00
	550	0.05	33.79	0.00	8.09	12.93	3.52	5.95	2.82	1.03	2.68	11.68	14.46	2.99	0.00	0.00	0.00	0.00
	600	0.00	34.78	0.00	3.18	12.47	4.16	7.70	2.55	1.19	2.86	10.75	14.51	5.85	0.00	0.00	0.00	0.00
	650	0.00	41.40	0.00	42.29	0.72	15.59	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

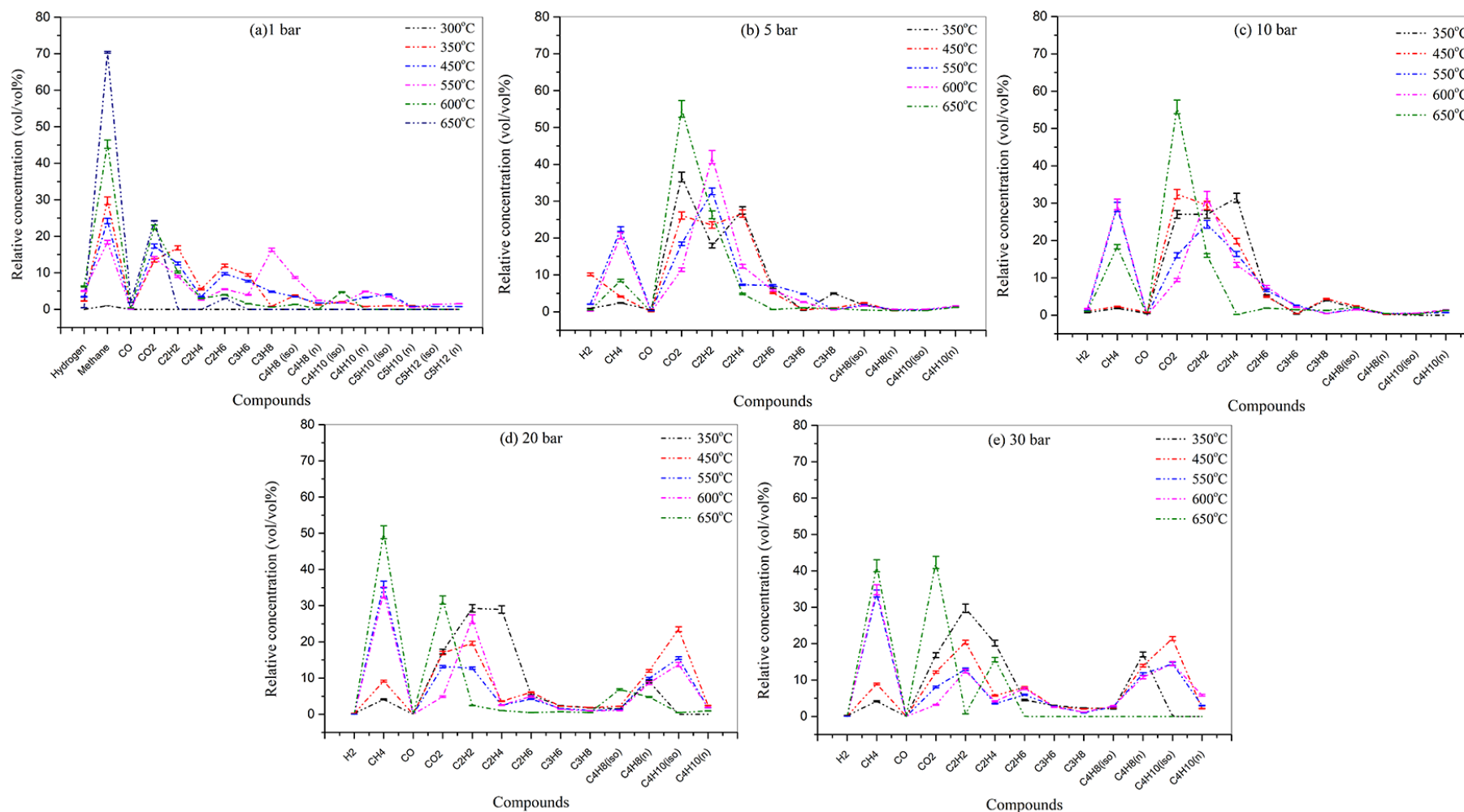


Fig 4.12. Relative concentration of permanent and hydrocarbon gases produced during pyrolysis of oil shale pyrolysis at 350, 450, 550, 600°C and 650°C after isothermal hold time of 2 hours under different operating pressures of (a) 1 bar, (b) 5 bar, (c) 10 bar, (d) 20 bar and (e) 30 bar.

4.4.2. Fourier transform infrared spectroscopy - attenuated total reflectance (FTIR-ATR) analysis

FTIR-ATR analysis was performed for the identification of probable functional groups in the pyrolytic shale oil samples obtained during the optimum run of High-pressure pyrolysis at 5, 10, 20, and 30 bar. The FTIR-ATR spectra of the pyrolytic oils obtained at 5, 10, 20, and 30 bar were compared with the oil obtained at atmospheric pressure (1 bar) and are presented in Fig 4.13. The assignment of wavenumber to different functional groups is tabulated in Table 4.4. The relative percentage of the identified functional groups were determined by calculation of the relative area of each function group. The quantification of the identified functional groups at each pyrolysis pressure with standard deviation values are summarized in Table 4.5. FTIR-ATR analysis of pyrolytic oil obtained at atmospheric pressure showed a broad hydroxyl group band from 3300 to 3500 cm^{-1} . The presence of aliphatic compounds was observed from 2500 to 3000 cm^{-1} with a sharp peak at 2950 cm^{-1} . The aromatic bending was observed from 680 to 860 cm^{-1} and 1480 to 1560 cm^{-1} , with sharp peaks at 692 and 1452 cm^{-1} . A minute peak was observed at 1600 cm^{-1} in the 20 and 30 bar spectra corresponding to weak aromatic C-H vibration. A broad band corresponding to phenols, alcohols, and ethers were observed from 933 to 1379 cm^{-1} with a sharp peak at 1140 cm^{-1} corresponding to phenolic compounds in the 5 bar and 10 bar spectra. The intensity of peak at 1140 cm^{-1} decreased significantly in the spectra for 20 and 30 bar. A broad peak corresponding to C=O stretch was observed from 1541 to 1768 cm^{-1} . The oil samples obtained from 5 bar to 30 bar showed complete absence of –OH group from 3300 to 3500 cm^{-1} and C=O group from 1541 to 1768 cm^{-1} . The decrease in some oxygen compounds with increase in pressure was previously observed by Burnham and McConaghy[64]. They observed that the concentration of fraction of H linked to α -heteroatoms decreased with increase in pressure. They showed that the concentration of ether decreased with increase in pyrolysis pressure from 1 bar to 53 bar. The concentration of phenolic and

carbonyl compounds decreased from 1 to 11 bar but increased at 53 bar. The phenolic concentration was reported to be higher at 53 bar as compared to 1 bar and the concentration of carbonyl compounds was lower at 53 bar than at 1 bar. Noble et al.[65] reported that at slow heating of Green River both the total oil yield and polar compounds decreased with increasing pyrolysis pressure. This supports our finding of a significant decrease in OH group compounds. Similar findings were reported by Salhi et al[215] who showed, that high pressure led to decrease in polar compounds.

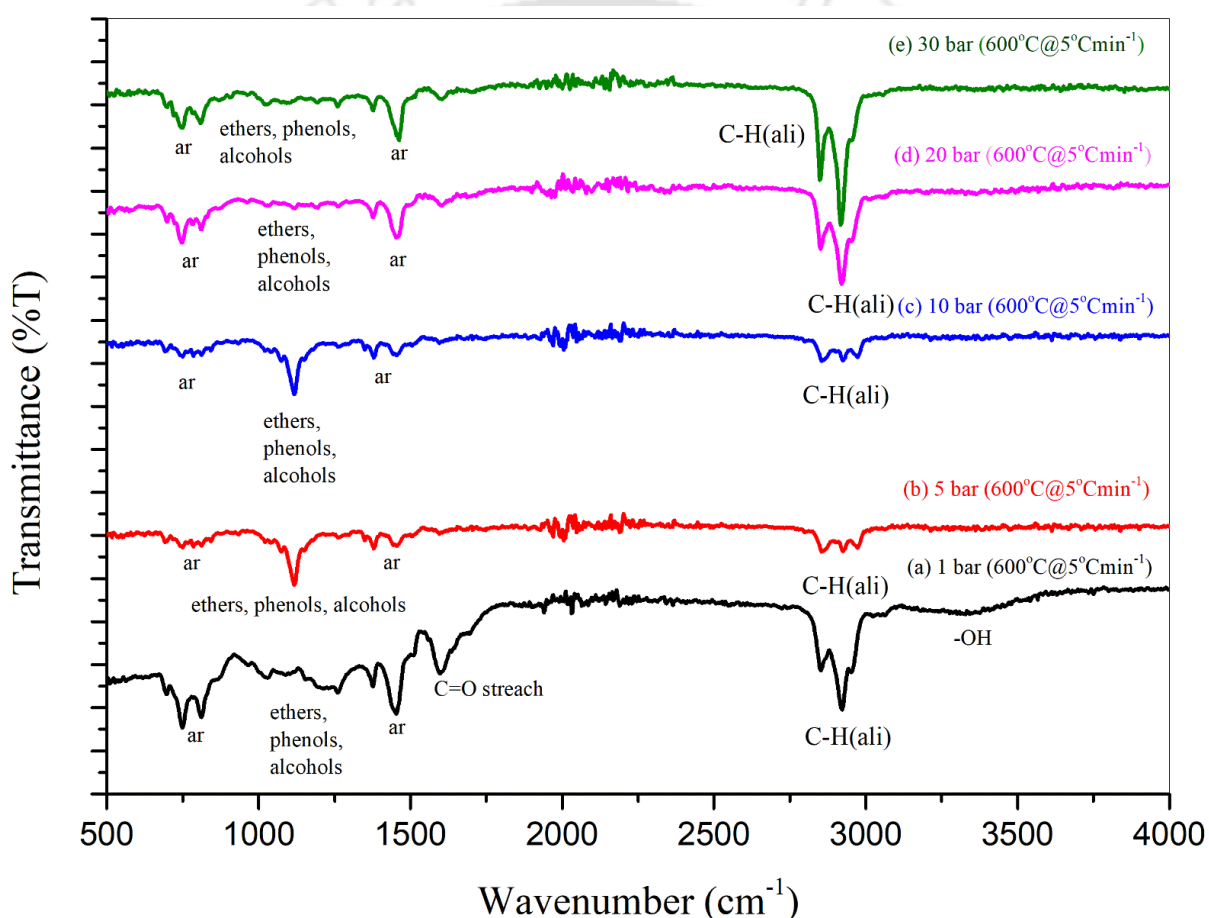


Fig 4.13. FTIR-ATR spectra of pyrolytic shale oil obtained at 600°C, at a heating rate of 5°C/min with isothermal holding time of 2 hours under operating pressure of (a) 1 bar, (b) 5 bar, (c) 10 bar, (d) 20 bar and (e) 30 bar. The spectra of pyrolytic oil obtained at elevated pressure of 5-30 bar showed absence of -OH group and C=O stretch at 3300-3500 cm⁻¹ and 1600 cm⁻¹ respectively.

Table 4.4. Functional groups corresponding to different wavenumbers.

Wavenumbers(cm^{-1})	Functional Groups
3625	-OH group; Alcohols and Phenols (strong; sharp)
3300-3500	-OH stretch from $-\text{COOH}$ and $-\text{COH}$
3000-2500	C-H stretch; Alkanes
1600-1650	Aromatics (Phenolic), $-\text{C}=\text{O}$ vibration; - C=O stretch from H-bonded conjugate
1400-1600	Aromatics
860-680	Aromatic C-H Stretch;
680-610	S-O bending; sulfates

Table 4.5. Relative concentration of identified functional groups.

Wavenumber (cm^{-1})	Functional Groups	1 bar (%)	5 bar (%)	10 bar (%)	20 bar (%)	30 bar (%)
3000	CH (aliphatic)	32.4 $\pm$ 1.1	50.4 $\pm$ 0.5	52.6 $\pm$ 0.8	54.3 $\pm$ 0.5	58.3 $\pm$ 0.8
3300	-OH	14.6 $\pm$ 1.3	0	0	0	0
1600	C=O	11.5 $\pm$ 0.7	0	0	0	0
1458	Aromatics	12.6 $\pm$ 0.5	10.5 $\pm$ 0.3	9.2 $\pm$ 0.5	9.7 $\pm$ 1.5	9.5 $\pm$ 1.3
1000-1200	Phenolic, ether and alcohol	16.7 $\pm$ 1.3	25.6 $\pm$ 1.6	27.3 $\pm$ 1.1	26.5 $\pm$ 1.8	23.4 $\pm$ 2.5
600-800	Aromatics	12. $\pm$ 1.9	13.3 $\pm$ 1.2	10.2 $\pm$ 1.2	9.2 $\pm$ 1.2	8.7 $\pm$ 1.6

The occurrence of 14.6% -OH group compounds in the oil obtained at 1 bar pressure may have appeared due to the presence of a small amount of residual aqueous phase in the oil sample as it is difficult to completely separate the aqueous phase from high viscosity oil sample.

4.4.3. Simulated distillation (SimDist) of pyrolytic oil

SimDist analysis of pyrolytic oil was performed to identify the distribution of carbon number in the optimum oil sample obtained at different operating pressure of 5, 10, 20, and 30 bar, and compared with oil sample obtained at 1 bar pressure. The concentration and standard deviation of each nominal carbon number are summarized in Table 4.6. The pyrolytic shale oil obtained under atmospheric pressure showed carbon number up to C₃₈, which summed up to 26.2% light distillates, 18.3% middle distillates, and 55.1% heavy distillates. However, the carbon number distribution decreased with increase in operating pressure. At 5 bar, the carbon number distribution was detected up to C₃₂ (28.1% light, 34.1% middle, and 42.9% heavy distillates). At 10 bar, the distribution decreased to C₃₀ (28.8% light, 34.6% middle, and 36.2% heavy distillates), at 20 bar, the distribution further decreased to C₂₆ (31.3% light, 35.8% middle, and 36.1% heavy distillates) and further reduced to C₂₂ at 30 bar pyrolysis pressure (45.3% light, 47.2% middle and 6.4% heavy distillates). The cumulative yield percentage of the carbon number distribution at different operating pressures (1, 5, 10, 20, and 30 bar) is illustrated in Fig 4.14 (a-b) showing the derived pyrolytic oil at high pressures to be abundant in gas-oil and kerosene fractions. The reduction in carbon number distribution can be associated with the reduction in density of pyrolytic oil with increase in pyrolysis pressure. The decrease in carbon number may have occurred because of the formation of lower molecular weight oil due to cracking and vaporization of oil at elevated temperature and pressure. Similar results were reported for SimDist data of High-pressure pyrolysis of Green River oil shale by Ryan et al.[218], and showed a reduction in molecular size of compounds with increase in pressure due to delayed oil vaporization and secondary cracking. Similar findings were also reported by

Burnham and McConaghy[64] who showed an increase in the occurrence of lower boiling point compounds with increase in pyrolysis pressure. This phenomenon was also explained by Burnham and Singleton[35] to occur due to the increase in residence time due to delay in oil-evolution or vaporization caused by high pressure.



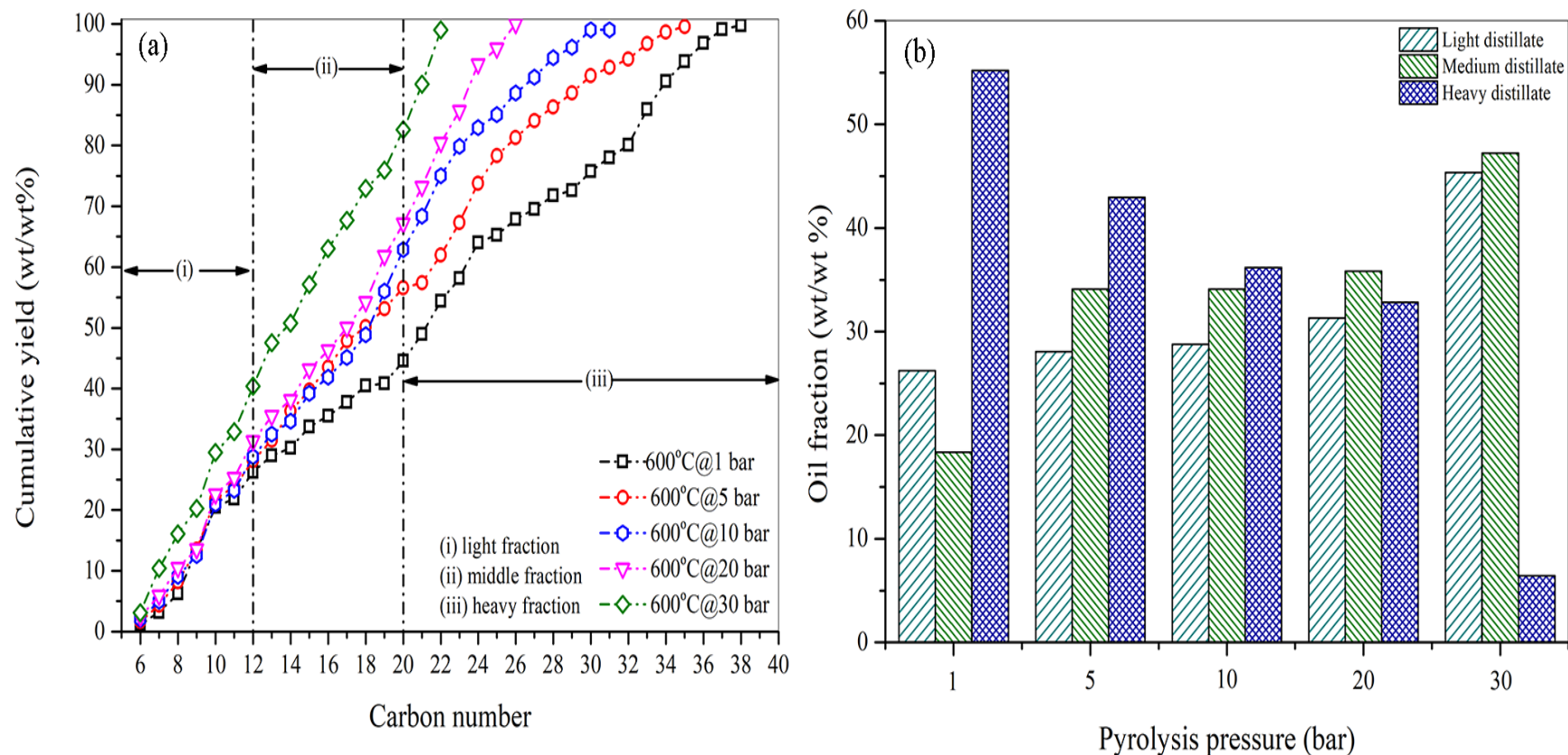


Fig 4.14. (a) Cumulative yield of hydrocarbons based on boiling point of compounds. (b) Fractional distribution of light, middle, and heavy distillates at different pyrolysis pressure. With increase in pyrolysis pressure, the carbon number distribution decreased, and the concentration of the distribution increased.

Table 4.6. Carbon number distribution as identified by SimDist analysis of pyrolytic oil samples obtained during pyrolysis at 1, 5, 10, 20, and 30 bar at temperature of 600°C, at heating rate of 5°C/min.

Carbon number distribution	1 bar (wt/wt%)	5 bar (wt/wt%)	10 bar (wt/wt%)	20 bar (wt/wt%)	30 bar (wt/wt%)
C ₆	1.1±0.05	1.6±0.1	2.0±0.07	2.4±0.05	3.1±0.1
C ₇	2.0±0.1	2.6±0.03	2.9±0.05	3.4±0	7.2±0.05
C ₈	3.0±0.2	3.8±0.05	4.0±0.1	4.5±0.05	5.6±0.1
C ₉	7.1±0.1	5.3±0.1	3.4±0.08	3.0±0.1	4.1±0.05
C ₁₀	7.1±0.1	8.3±0.09	0.4±0.09	9.0±0.15	2.1±0.05
C ₁₁	1.3±0.1	1.9±0.15	2.2±0.05	2.7±0.1	3.4±0.03
C ₁₂	4.3±0.1	5.2±0.05	5.5±0.02	6.0±0.05	7.4±0.09
C ₁₃	2.7±0.1	3.4±0.05	3.7±0.08	4.1±0.03	7.2±0.1
C ₁₄	1.2±0.02	4.7±0.03	2.1±0.05	2.5±0.03	3.2±0.05
C ₁₅	3.5±0.04	3.4±0.05	4.6±0.1	5.1±0.02	6.3±0.05
C ₁₆	1.7±0.1	3.7±0.05	3.6±0.05	3.1±0.07	11.8±0.05
C ₁₇	2.2±0.05	4.3±0.05	3.2±0.1	3.7±0.15	4.6±0.1
C ₁₈	2.7±0.05	2.3±0.1	3.7±0.05	4.1±0.03	5.2±0.07
C ₁₉	0.3±0.05	2.9±0.07	7.1±0.1	9.6±0.09	3.0±0.1
C ₂₀	3.7±0	3.4±0.09	6.8±0.05	5.3±0.1	6.6±0.07
C ₂₁	4.4±0.01	0.8±0.03	5.5±0.02	6.0±0.05	7.5±0.05
C ₂₂	5.4±0.03	4.5±0.08	6.6±0.03	7.2±0	8.9±0.05
C ₂₃	3.7±0.1	5.3±0.1	4.1±0.2	5.3±0.02	-
C ₂₄	5.8±0.1	6.4±0.05	7.0±0.09	7.6±0.09	-
C ₂₅	1.2±0.1	4.5±0.09	2.1±0.08	2.5±0.05	-
C ₂₆	2.5±0.05	6.9±0.1	3.5±0.03	4.0±0.02	-
C ₂₇	1.6±0.1	2.7±0.1	2.6±0.05	-	-
C ₂₈	2.2±0.1	3.2±0.05	3.1±0.07	-	-
C ₂₉	0.8±0.05	2.2±0.05	1.7±0.05	-	-
C ₃₀	3.1±0.1	2.8±0.08	2.8±0.1	-	-

C ₃₁	2.2±0.2	1.3±0.05	-	-	-
C ₃₂	2.0±0.1	1.3±0.05	-	-	-
C ₃₃	5.8±0.05	2.5±0.03	-	-	-
C ₃₄	4.5±0.4	3.9±0.05	-	-	-
C ₃₅	3.2±0.05	2.9±0.2	-	-	-
C ₃₆	3.0±0.05	-	-	-	-
C ₃₇	2.2±0.1	-	-	-	-
C ₃₈	1.0±0.1	-	-	-	-

4.4.4. Nuclear magnetic resonance (¹H NMR) spectroscopy analysis

The ¹H NMR spectra of pyrolytic oils obtained at different pyrolysis pressure are shown in Fig 4.15. The quantification of different functional groups with standard deviation is tabulated in Table 4.7. Previous investigation of the composition of pyrolytic oil obtained at 1 bar pressure showed 36% straight-chain moieties, 29% unsaturated aliphatics, and α-heteroatoms, 10% α-CH₂ and α-CH₃ to aromatics, and 21% aromatics (Figure 4.15(a))[22]. The chemical shift obtained for ¹H NMR of shale oil obtained at 5, 10, 20, and 30 bar appeared to be rich in aliphatic compounds. The integral area showed 50%, 54%, 58.2%, and 61% of straight-chain moieties respectively. The NMR spectra corresponding to aliphatic compounds have been shown in a magnified scale from 0.5 - 1.2 ppm to show the distribution of different aliphatic protons (Fig 4.16 (a-d)). The percentage of unsaturated aliphatics and α-heteroatoms or unsaturated aliphatics was found to be 16% at 5 bar, 14% at 10 bar, and decreased to 12% at 20 bar and 30 bar. The percentage of α-CH₂ and α-CH₃ to aromatics increased with increase in pyrolysis pressure from 5 bar to 30 bar. The multiplets occurring around 3.3 ppm are shown in Fig 4.17 (a-d). The integral area was recorded to be fairly consistent at 19% at 5 bar and 20%, at 10, 20, and 30 bar. The quantification of aromatics were recorded to be 15% (5 bar), 12% (10 bar), 10% (20 bar) and 7% (30 bar). The decrease in the percentage of aromatic compounds

occurs due to coking reactions at elevated pressure (Figure 4.15(b-e)). The coking of aromatics can be observed by calculating the changes in total group molecular weight (T_w) (g/mol), total group molecular weight of aromatics (A_w) (g/mol), and total aromatic content (A_c) (wt/wt %), in the samples by using correlations provided by Kumar et al. [10]. The quantification of T_w , A_w , and A_c with standard deviation are presented in Table 4.8. It was observed that T_w decreased with increase in pyrolysis pressure from 1 bar to 30 bar. The reduction in total group molecular weight corresponded by the decrease in carbon numbers distribution in pyrolytic oil samples observed by SimDist analysis. The coking of aromatic compounds is exemplified by the reduction in A_w to 240, 187, 143, and 117 for 5, 10, 20, and 30 bar, respectively compared to 335 g/mol at 1 bar. Moreover, A_c was found to be 22, 16, 13, 11, and 9 wt% at 1, 5, 10, 20, and 30 bar respectively. The increase in aliphatic compounds may have occurred due to hydrogenation of aromatic compounds at high pressure. Higher percentage of aliphatic compounds increased the research octane number (RON) in the pyrolytic oil. RON was determined by the correlations provided by Meyers et al.[219] to be 84, 86, 86, and 88 at 5, 10, 20, and 30 bar respectively compared to 83 of the pyrolytic oil obtained at 1 bar pyrolysis pressure. High pressure leads to an increase in the volatilization temperature of hydrocarbons leading to delay in hydrocarbon expulsion and decreased rate of vaporization. The increase in residence time increases the cracking of straight-chain moieties due to prolonged exposure to secondary reactions[64]. This also leads to the occurrence of enhanced cracking and coking reactions of aromatics, leading to decrease in aromatic percentage in the pyrolytic oil sample.

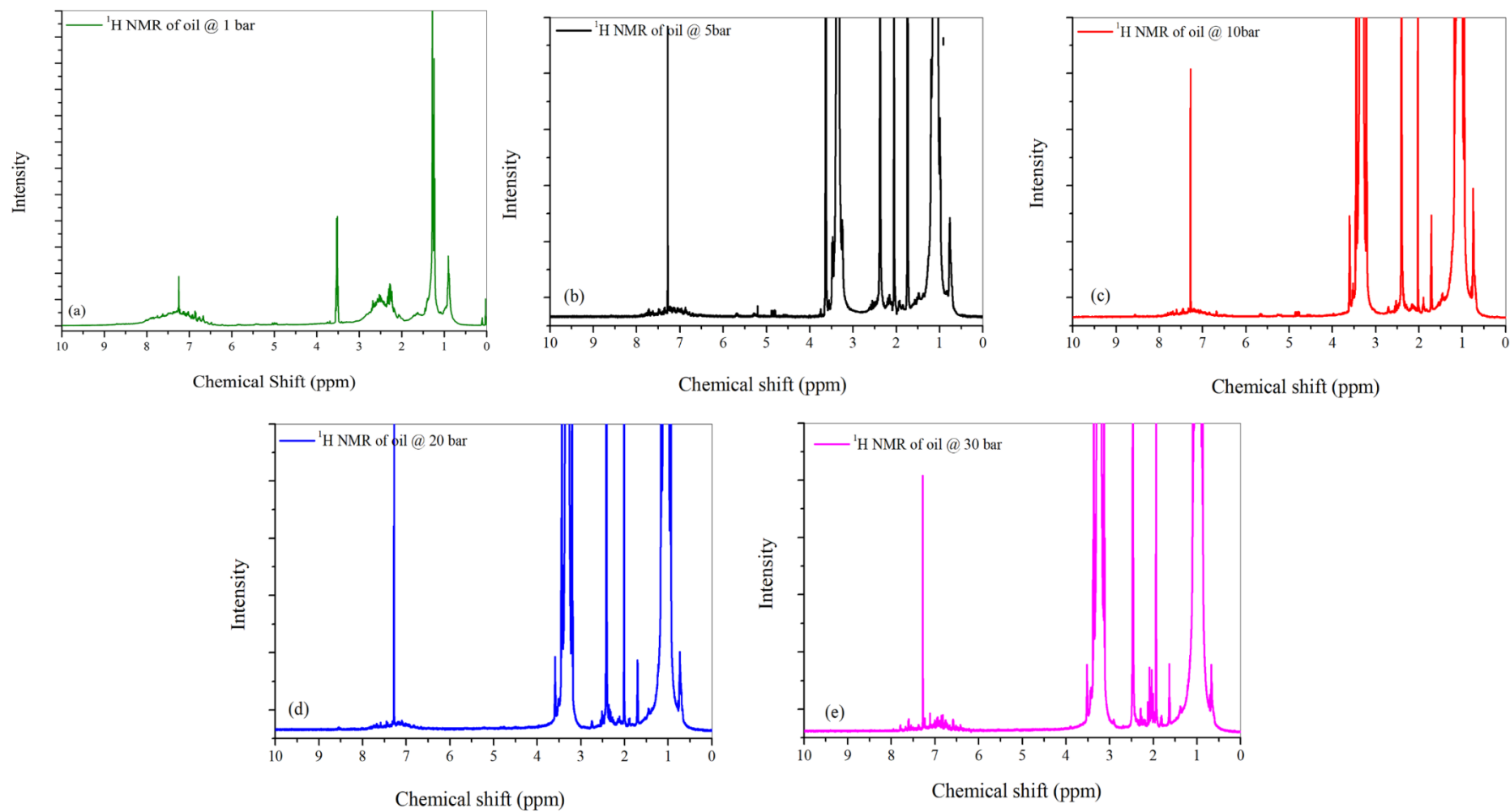


Fig 4.15. ^1H NMR spectra of pyrolytic oil obtained at (a) 1 bar [22], (b) 5 bar, (c) 10 bar, (d) 20 bar, and (e) 30 bar at $5^\circ\text{C}/\text{min}$ and 600°C .

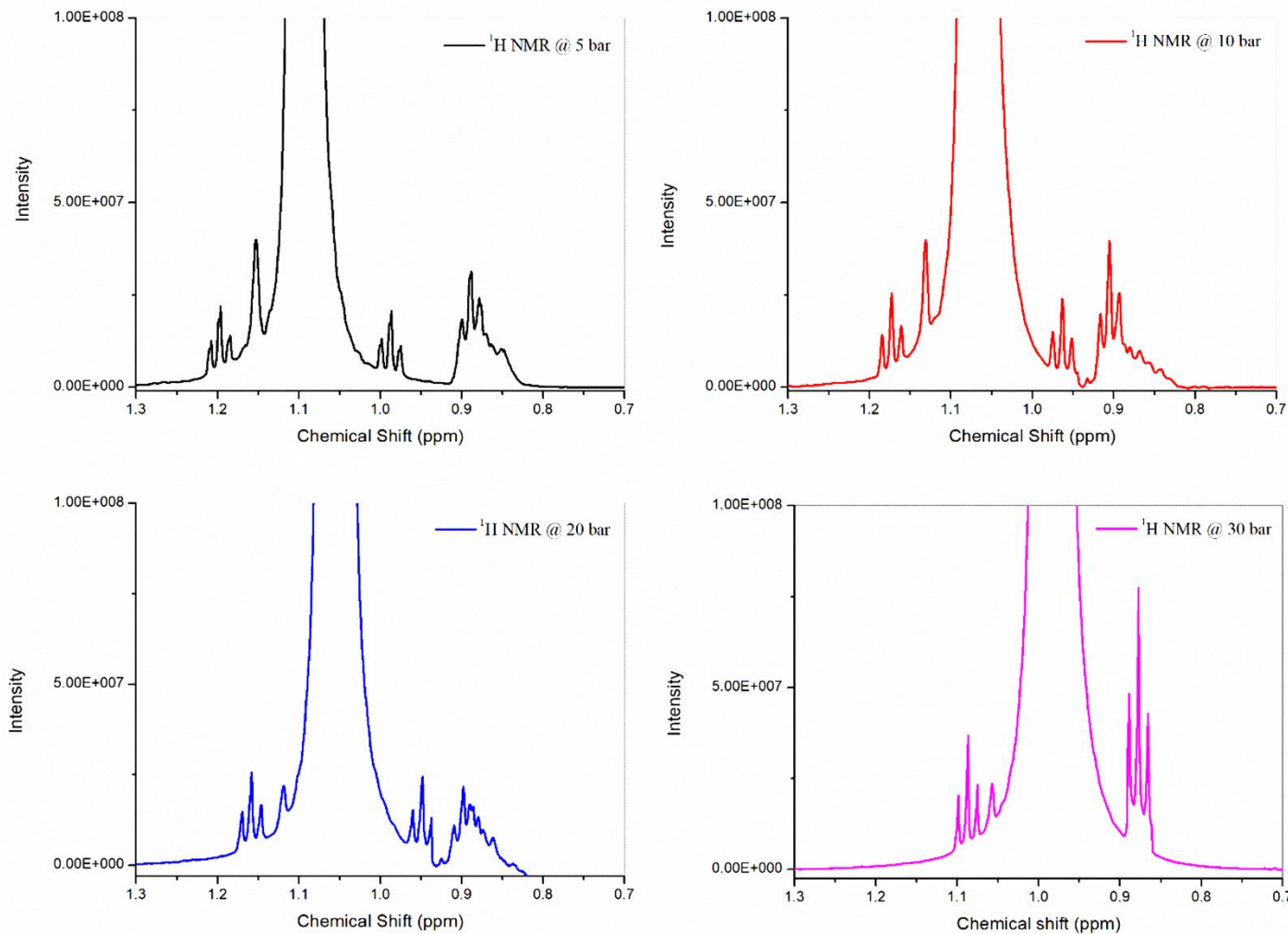


Fig 4.16. ^1H NMR spectra from 0.7 ppm to 1.3 ppm showing shift in methyl group with increase in pyrolysis pressure.

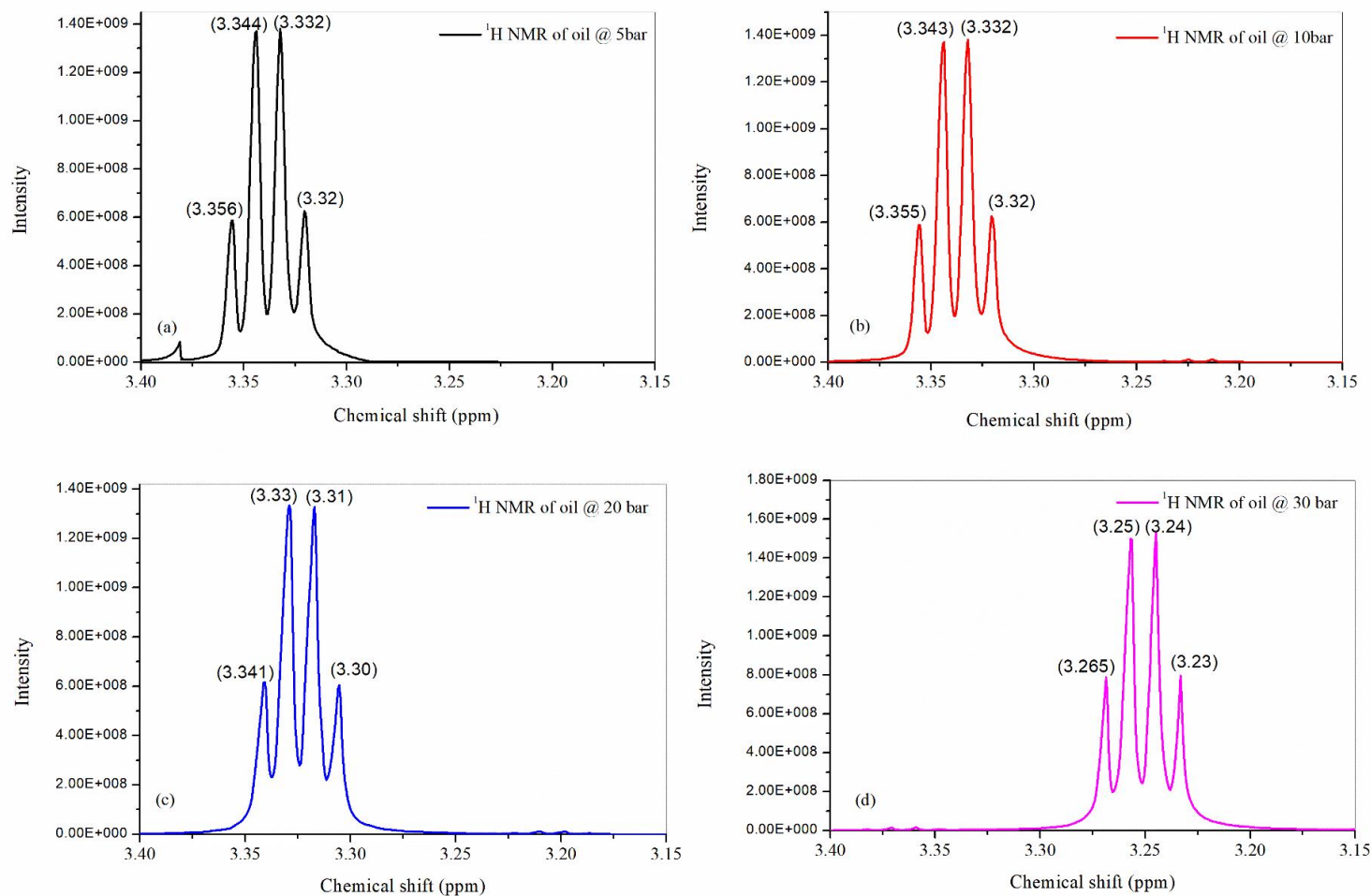


Fig 4.17. ^1H NMR spectra from 3 ppm to 3.4 ppm showing the shift of the multiplets in the $\alpha\text{-CH}_2$ and $\alpha\text{-CH}_3$ to aromatic group with increase in pyrolysis pressure.

Table 4.7. Percentage of compounds determined by ^1H NMR of pyrolytic oils obtained High-pressure pyrolysis at isobaric pressures of 5, 10, 20 and 30 bars at pyrolysis temperature of 600°C , at a heating rate of $5^\circ\text{C}/\text{min}$ and comparison with oil obtained at atmospheric (1 bar) pressure.

Proton Assignment (^1H)	1 bar (%) [22]	5 bar (%)	10 bar (%)	20 bar (%)	30 bar (%)
Alkanes (0.3-1.9 ppm)	36 $\pm$ 2	50 $\pm$ 1	54 $\pm$ 1.5	58 $\pm$ 2.2	61 $\pm$ 1.5
Aliphatics α -heteroatoms or unsaturations (1.9-3 ppm)	29 $\pm$ 1	16 $\pm$ 2	14 $\pm$ 1	12 $\pm$ 0.3	12 $\pm$ 1
α -CH ₂ and α -CH ₃ to aromatic (3-4.5 ppm)	10 $\pm$ 1	19 $\pm$ 1	20 $\pm$ 0.5	20 $\pm$ 1	20 $\pm$ 0.5
Methoxys and carbohydrates (4.5-6 ppm)	3 $\pm$ 0.5	0	0	0	0
Aromatic (6-8.5 ppm)	21 $\pm$ 0.8	15 $\pm$ 0.9	12 $\pm$ 0.8	10 $\pm$ 0.8	7 $\pm$ 1.7
Esters and carboxylic acids (8.5-10 ppm)	1 $\pm$ 0	0	0	0	0

Table 4.8. Identification of total group molecular weight, total group molecular weight of aromatic compounds, total aromatic content and research octane number for pyrolytic oil obtained at 1, 5, 10, 20, and 30 bar pyrolysis pressure.

Parameters	1 bar	5 bar	10 bar	20 bar	30 bar
Total group molecular weight of sample (g/mol)	1489 $\pm$ 0.6	1432 $\pm$ 0.1	1373 $\pm$ 0.5	1292 $\pm$ 0.4	1198 $\pm$ 0.2
Total group molecular weight of aromatic compounds (g/mol)	335 $\pm$ 0.5	240 $\pm$ 0.5	187 $\pm$ 0.6	143 $\pm$ 0.6	117 $\pm$ 0.5
Total aromatic content (wt %)	22 $\pm$ 0.4	16 $\pm$ 0.7	13 $\pm$ 0.3	11 $\pm$ 0.6	9 $\pm$ 0.2
Research octane number	83 $\pm$ 0.05	84 $\pm$ 0.5	86 $\pm$ 0.05	86 $\pm$ 0.2	88 $\pm$ 0.05

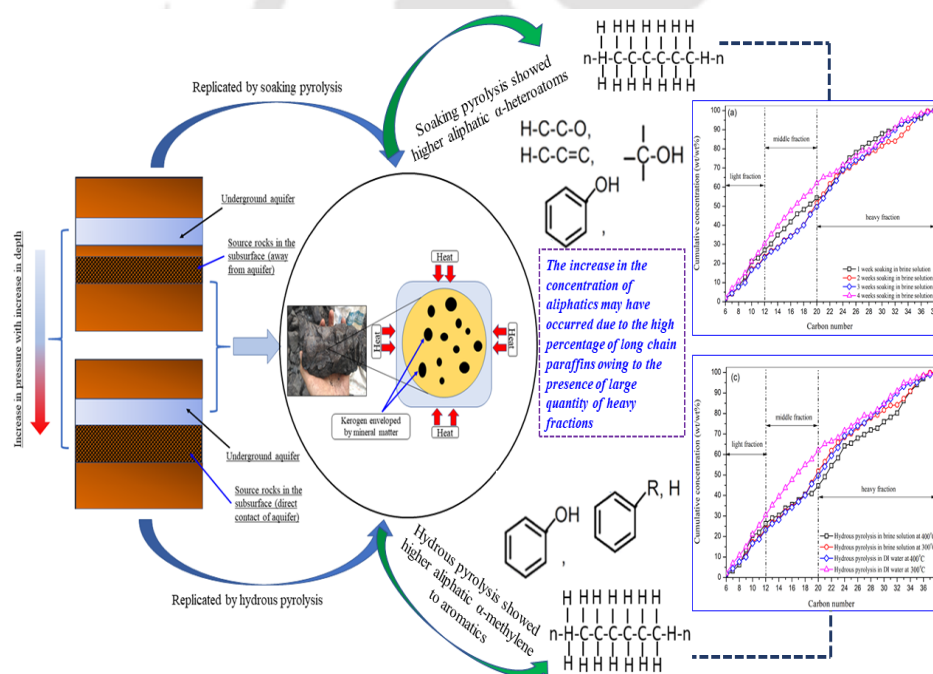
4.5. Conclusive summary

High-pressure thermogravimetric analysis of oil shale pyrolysis showed increase in volatilization temperature of hydrocarbons with increase in pyrolysis pressure. Kinetic study of oil shale pyrolysis under high pressure showed the mean apparent activation energy to increase from 247.5 kJmol⁻¹ at 1 bar to 434, 443, and 451 kJmol⁻¹ at 5, 10, and 20 bar respectively, but decreased to 341 kJmol⁻¹ at 30 bar. High-pressure kinetics showed the occurrence of three-reaction model; D3 diffusion at low conversions, F2 second order reaction at intermediate conversions and A3 Avrami Eroffev model at higher conversions. The effect of vaporization of oil due to cracking and the occurrence of secondary reactions were observed with the decrease of oil yield and an increase in gas yield with an increase in pyrolysis pressure. The relative concentration of C₂-C₄ gases obtained at high pressure increased dramatically compared to atmospheric pressure. SimDist analysis showed an increase in the percentage of lighter (gasoline) and middle (kerosene) fractions from 26.2 wt/wt% and 18.3 wt/wt% at 1 bar to 45.3wt/wt % and 47.2 wt/wt% at 30 bar respectively categorizing in the gasoil and kerosene section of distillates. FTIR and ¹H NMR analysis showed a significant decrease in the concentration of aldehydes, ketones, carboxylic acids, and aromatics and an increase in concentration of alkanes at high pressure. The decrease in the percentage of aromatics occurs due to enhanced cracking and coking reactions at high pressure. The RON of oil sample increased from 83 at 1 bar to 88 at 30 bar. This indicated that the conditions of high pressure and high temperature lead to in-situ thermal cracking and reforming, resulting in the formation of abundant light and middle distillates. At these conditions, the Indian oil shale possesses the potential to be an important source of high-value fuels.

Chapter 5

Soaking and hydrous pyrolysis of Indian oil shale: Identification of produced hydrocarbons and moieties

- Soaking pyrolysis
- Hydrous pyrolysis
- Brine solution
- De-ionized water
- Product characterization



Published as:

B. Baruah and P. Tiwari, "Soaking and hydrous pyrolysis of Indian oil shale: Identification of produced hydrocarbons and moieties", **Fuel**, Elseviers, 322, doi.org/10.1016/j.fuel.2022.124255, 2022.

5. Soaking and hydrous pyrolysis

Various techniques have been reported to measure oil and gas generation kinetics for kerogen pyrolysis, although the detailed information for individual pyrolysis products is not provided adequately. The latter is of significant importance to provide an insight into the possible structure of kerogen and understand the expulsion ratio of oil to gas during the maturation of kerogen. This information will further help establish the cause of the variation in activation energy distribution and modeling of secondary reactions in the presence of inherent minerals [220]. Also, the presence of water during pyrolysis increases the pressure due to steam formation and may also act as a source of hydrogen and thereby influence the composition and yield of the produced oil and gases. Additionally, if water is associated with the organic matter in the oil shale or source rock samples, the solubilities of different organic substances produced during in-situ pyrolysis process may lead to contamination of water bodies and lead to environmental issues[8]. To address the same, the current chapter aims to present a detailed study on the generation of hydrocarbons during thermal degradation of Indian oil shale in the presence of de-ionized (DI) water and brine solution. These experiments attempt to simulate the in-situ maturation of source rocks in direct and indirect contact with pure and high-salinity underground aquifers water.

5.1. Lab scale pyrolysis experiments

To design the experimental study, two sets of experiments were prepared. Firstly, the oil shale samples were soaked in DI water and brine water separately for a duration of 1 to 4 weeks before pyrolysis. In the second set of experiments, the oil shale samples were subjected to hydrous pyrolysis by adding DI water and brine solution, separately to the oil shale sample in the pyrolysis reactor and heated isothermally. DI water was used as a reference to study the effect of brine solution in the composition of the obtained pyrolytic oil and gas. The methodology of the Soaking and hydrous pyrolysis experiments has been described intricately in section 2.12.3 of Chapter 2 (Materials and methodology). The produced oil and gases were characterized to identify the generation of short chain and long chain hydrocarbons, and the production of organic acids during the maturation of kerogen into oil and gas. The condensed aqueous phase was analyzed to measure the alteration in the composition of the water phase because of the solubility of the organics produced during pyrolysis. The yields of oil, gas and spent shale for Soaking and hydrous pyrolysis experiments in both brine solution and DI water are reported in Table 5.1-5.3. The oil yield increased with increase in pyrolysis temperature (from 300 to 400°C) for both soaking and hydrous pyrolysis experiments. This may have occurred because, during hydrous pyrolysis the expulsion of bitumen occurs around at 300°C, and the pyrolytic bitumen gets converted into subsequent hydrocarbon oil and gas at after 350°C [76, 221]. For soaking pyrolysis, the maximum reached pressure was 90 bar, and for hydrous pyrolysis experiments the maximum pyrolysis pressure was recorded as 125 bar. Increase in soaking time has no change in the total mass loss of the oil shale sample during pyrolysis.

5.1.1. Soaking pyrolysis experiments

The schematic diagram for soaking pyrolysis experiments is shown in Fig 2.6 (a) of Materials and methodology. For 1-week soaking time in DI water the oil yield increased from 6.38

vol/wt% to 8.17 vol/wt% with increase in pyrolysis temperature from 300 to 400°C. Similarly, for soaking time of week 2, 3, and 4 the oil yield was recorded to increase from 6.34 vol/wt% to 8.27 vol/wt%, 6.96 vol/wt% to 8.47 vol/wt%, and 6.79 vol/wt% to 8.46 vol/wt%, respectively. Again, for 1-week soaking time in brine solution the oil yield increased from 7.05 vol/wt% to 8.35 vol/wt% with increase in pyrolysis temperature from 300 to 400°C. Similarly, for soaking time of week 2, 3, and 4 the oil yield was recorded to increase from 7.1 vol/wt% to 8.51 vol/wt%, 7.65 vol/wt% to 8.71 vol/wt%, and 7.42 vol/wt% and 8.82 vol/wt%, respectively. With increase in soaking duration the yield of aqueous phase increased from week 1 to week 4 (Table 5.1-5.2), which may have been because of the presence of excess amount of absorbed water in the surface of the oil shale. Although, with increase in soaking time the mass loss and oil yield increased with increase in pyrolysis temperature from 300 °C to 400°C, the gas yield decreased from 300°C to 350°C, and increased at 400°C.

5.1.2. Hydrous pyrolysis experiments

The schematic diagram for soaking pyrolysis experiments is shown in Fig 2.6 (b) of Chapter 2. For hydrous pyrolysis experiments using brine solution, the oil yield increased with increase in pyrolysis temperature from 300°C to 400°C, and a sharp decrease was observed in the gas yield. However, the oil and gas yield during hydrous pyrolysis experiments in DI water showed similar trend to the soaking pyrolysis. Hydrous pyrolysis produced a maximum oil yield of 7.03 vol/wt%, and 6.81 vol/wt% in brine solution and DI water respectively at pyrolysis temperature of 400°C. The slight increment in oil yield in DI water as compared to brine solution is not sufficient to justify the increase in oil yield in the presence of DI water as compared to mineral dissolved water (brine solution). Gas yield of 4.31 vol/wt% and 3.68 vol/wt% was observed for hydrous pyrolysis in brine solution and DI water, respectively at 300°C. However, it was observed that the gas yield increased to 4.79 vol/wt% for pyrolysis in brine water at 400°C, and 5.26 vol/wt% for pyrolysis in DI water at 400°C. Previous studies

on hydrous pyrolysis of kerogen samples reported an increasing-decreasing trend in oil yield with an increase in water pressure from 50 bar to 500 bar, and 500 bar to 800 bar at pyrolysis temperature of 375°C for a residence time of 48 hours[222]. As the generation of hydrocarbons is prominent above 350°C, the oil and gas samples obtained at pyrolysis temperature of 400°C have been considered for characterization.



Table 5.1. Yield of pyrolysis products during soaking pyrolysis in DI water.

Soaking time	Temperature (°C)	weight loss (wt/wt%)	Oil yield (wt/wt%)	Aqueous phase (wt/wt%)	Gas yield (wt/wt%)	Spent shale (wt/wt%)
1 week	400	13.77±0.65	8.17±0.24	3.04±0.10	2.56±0.25	86.23±0.68
	350	12.94±0.42	6.66±0.31	3.21±0.15	2.07±0.34	87.06±0.47
	300	12.31±0.66	6.38±0.25	3.55±0.09	2.38±0.27	87.69±0.69
2 weeks	400	14.76±0.21	8.27±0.27	3.10±0.11	3.39±0.30	85.24±0.25
	350	13.04±0.43	7.73±0.22	3.20±0.12	2.10±0.25	86.96±0.43
	300	12.72±0.61	6.34±0.28	3.64±0.05	2.74±0.31	87.28±0.63
3 weeks	400	15.26±0.27	8.47±0.20	3.10±0.06	3.70±0.22	84.74±0.30
	350	13.67±0.54	6.84±0.38	3.22±0.12	2.61±0.42	86.33±0.55
	300	11.45±0.59	6.96±0.33	3.56±0.11	0.93±0.35	88.55±0.58
4 weeks	400	15.58±0.66	8.46±0.36	3.21±0.07	3.91±0.32	84.42±0.65
	350	13.36±0.58	7.41±0.49	3.50±0.05	2.44±0.53	86.64±0.56
	300	12.72±0.47	6.79±0.61	3.50±0.10	2.43±0.58	87.28±0.45

Table 5.2. Yield of pyrolysis products during soaking pyrolysis in brine solution.

Soaking time	Temperature (°C)	Weight loss (wt/wt%)	Oil yield (wt/wt%)	Aqueous phase (wt/wt%)	Gas yield (wt/wt%)	Spent shale (wt/wt%)
1 week	400	14.43±0.67	8.35±0.32	3.85±0.05	3.08±0.33	85.57±0.66
	350	13.57±0.51	7.01±0.21	4.15±0.08	2.56±0.24	86.43±0.50
	300	12.90±0.47	7.05±0.24	4.20±0.10	2.85±0.22	87.10±0.45
2 weeks	400	15.47±0.54	8.51±0.35	4.88±0.08	3.96±0.34	84.53±0.53
	350	13.67±0.61	7.07±0.23	4.20±0.10	2.60±0.25	86.33±0.61
	300	13.33±0.42	7.10±0.27	4.20±0.07	3.23±0.42	86.67±0.41
3 weeks	400	16.00±0.10	8.71±0.31	3.88±0.10	4.29±0.34	84.00±0.31
	350	14.33±0.63	7.20±0.43	4.20±0.07	3.13±0.44	85.67±0.61
	300	12.00±0.52	7.65±0.58	4.20±0.05	1.35±0.60	88.00±0.54
4 weeks	400	16.33±0.05	8.82±0.55	3.21±0.05	4.51±0.54	83.67±0.07
	350	14.00±0.22	7.05±0.32	4.50±0.10	2.95±0.32	86.00±0.28
	300	13.33±0.56	7.42±0.45	3.50±0.12	2.91±0.45	86.21±0.60

Table 5.3. Yield of pyrolysis products during hydrous pyrolysis experiments in brine solution and DI water for 72 hours.

Water/solution	Temperature (°C)	Weight loss (wt/wt%)	Oil yield (wt/wt%)	Gas yield (wt/wt%)	Spent shale (wt/wt%)
DI water	400	12.07±0.57	6.81±0.28	5.26±0.21	87.93±0.60
	350	10.79±0.48	6.60±0.31	4.19±0.33	89.21±0.54
	300	10.30±0.61	6.62±0.22	3.68±0.24	89.7±0.60
Brine solution	400	11.82±0.32	7.03±0.35	4.79±0.36	88.18±0.30
	350	10.87±0.45	6.56±0.31	4.31±0.27	89.13±0.47
	300	10.68±0.55	6.36±0.21	4.31±0.33	89.32±0.56

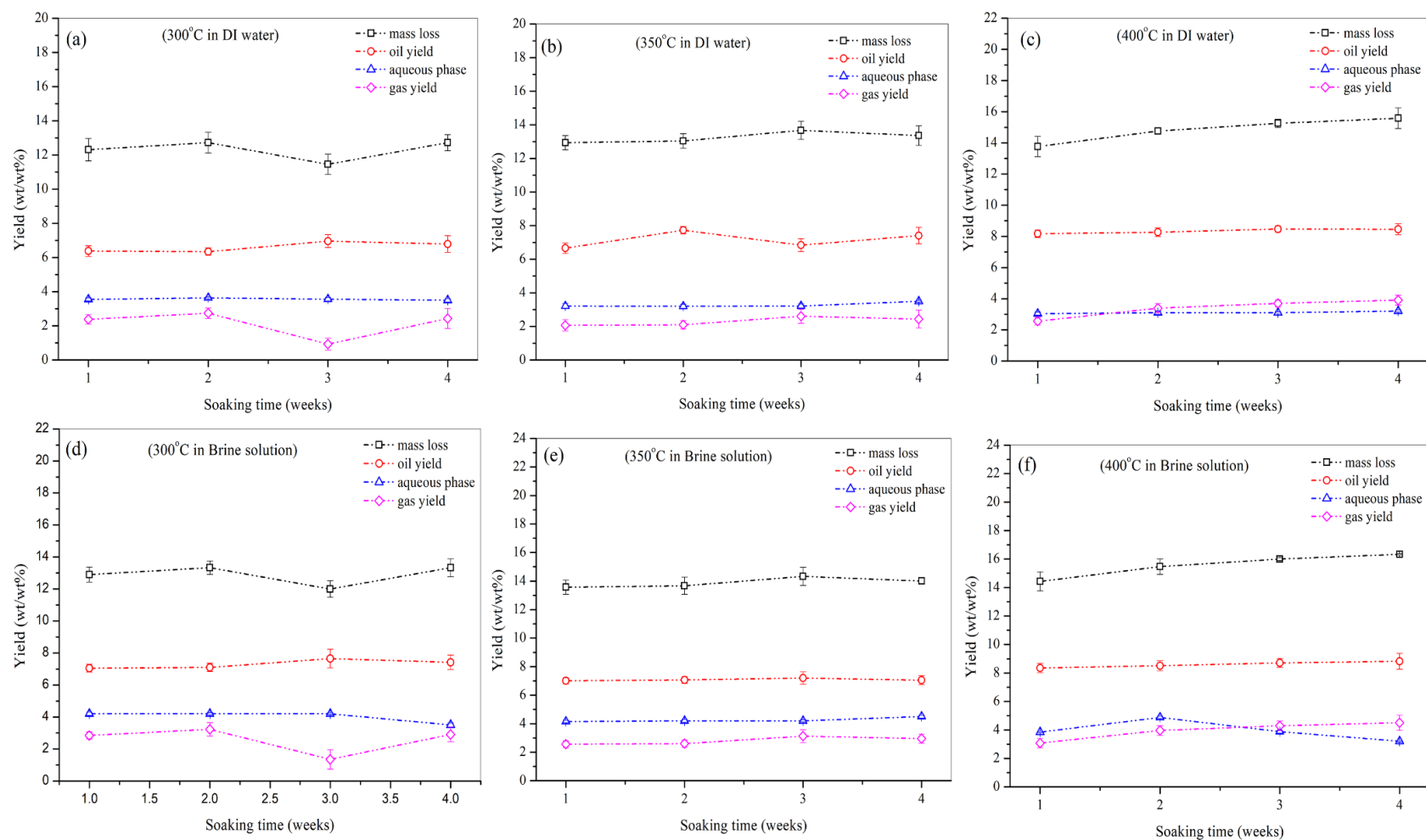


Fig 5.1. Distribution of product yield during soaking pyrolysis in DI water and brine solution at pyrolysis temperatures of (a) 400°C, (b) 350°C, and (c) 300°C, and in brine solution at (d) 400°C, (e) 350°C, and (f) 300°C.

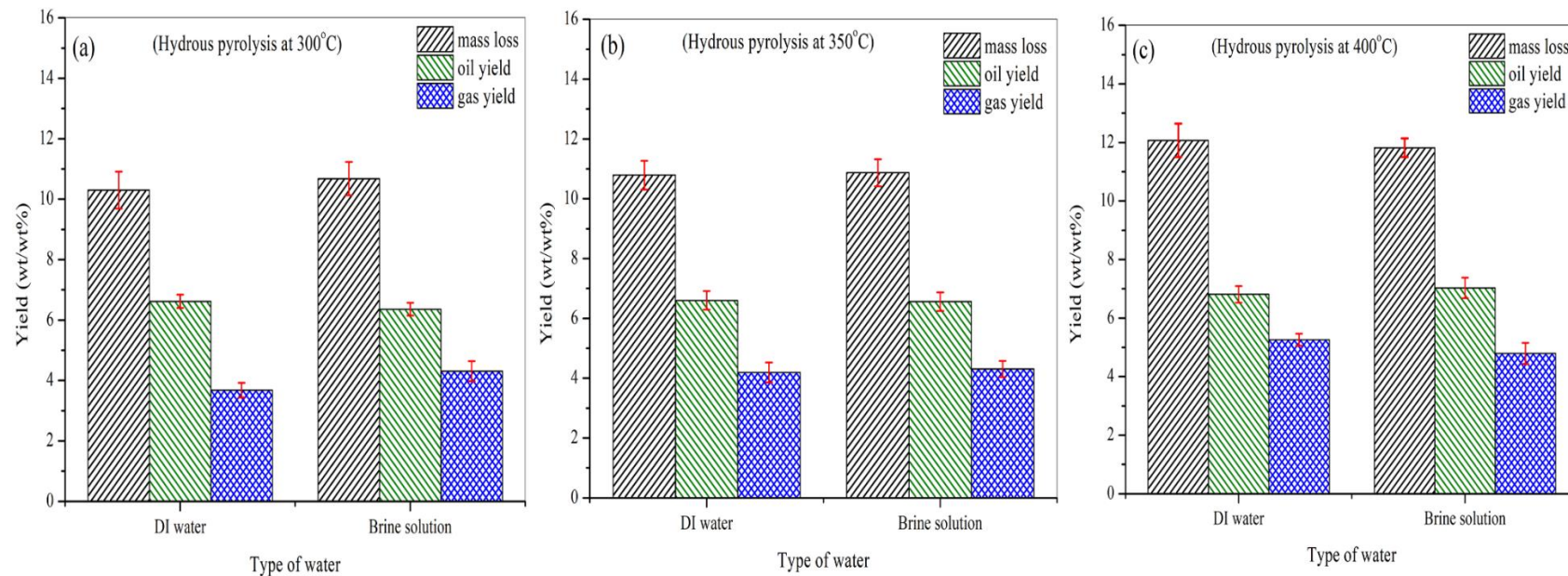


Fig 5.2. Distribution of yield during hydrous pyrolysis in DI water and brine solution at (a) 400°C, (b) 350°C, and (c) 300°C.

5.2. Characterization of pyrolytic products

5.2.1. Gas-Chromatography of gaseous products

Quantification of the produced gases during soaking and hydrous pyrolysis experiments showed the presence of gases from C₁ to C₅. The relative concentrations of the identified gases are presented in Fig 5.3 – 5.5 and tabulated in Table 5.4 and 5.5. At 300°C with the formation of pyro-bitumen, soaking pyrolysis in brine solution showed that the concentration of CO₂ and CH₄ increased with an increase in soaking time from 1 to 4 weeks. Conversely, the concentration of CO₂ decreased from 350°C to 400°C, but the trend of CH₄ did not change. However, for soaking pyrolysis in DI water, the concentration of CO₂ decreased with an increase in soaking time, and methane increased with soaking time along with an increase in pyrolysis temperature from 300°C to 400°C. The concentration of gases from C₂ to C₅ decreased with an increase in temperature from 300°C to 400°C for soaking in both brine and DI water. However, an increase in soaking time for brine solution increased the concentration of C₄ to C₅ gases compared to soaking in DI water from 300°C to 400°C. The increase in the concentration of the hydrocarbon gases from C₄ and C₅ may have been because after 350°C the pyro-bitumen undergoes cracking reactions, leading to the formation of lighter hydrocarbon products[76]. A minute concentration of H₂ was found to appear in soaking pyrolysis experiments in both DI water and brine solution. This is because the presence of water during pyrolysis acts as a hydrogen donor and is used up in the alkylation reactions leading to the generation of straight-chain alkanes[83]. The presence of CO was found to be negligible in all the gas samples. The gas samples collected from hydrous pyrolysis in brine solution and DI water showed that the concentration of CO₂ increased from 300°C to 350°C but decreased from 350°C to 400°C. The concentration of H₂ appeared to increase from 300°C to 350°C and then decrease from 350°C to 400°C. The concentration of methane increased with an increase in temperature from 300°C to 400°C, along with C₂ and C₃ gases. The concentration of C₄ and C₅

gases showed a sharp increase with an increase in pyrolysis temperature from 300°C to 400°C in the presence of both brine solution and DI water. The increase in CH₄ and C₂-C₅ gases concentration was also observed by Wu et al.[81] during hydrous pyrolysis of type-I kerogen in the pressure range of 50 bar to 190 bar. The increase in the concentration of C₄ and C₅ gases with an increase in temperature was also observed in our previous study during anhydrous High-pressure pyrolysis[72]. The formation of methane occurs with the conversion of kerogen into bitumen around 300°C [223] and due to the cracking of C₂ gases at higher temperatures[224]. Methane is produced predominantly by the initial cracking of kerogen at low maturity. And again, at higher levels of thermal maturity, the abundance of methane increases due to the cracking of bitumen[225]. The abundance of CO₂ and CH₄ gases in gas samples obtained from hydrous pyrolysis experiments, was previously noticed by Kanuss et al. [79]. The dominance of CO₂ during hydrous pyrolysis of different oil shale and coal samples around the world have been extensively reported in the literature reported[226-228].

Table 5.4. Relative concentration of hydrocarbon and permanent gases obtained from soaking pyrolysis in brine solution and DI water separately at isothermal pyrolysis temperature of 300°C, 350°C, and 400°C.

Time (week)	Temp (°C)	H ₂ (%)	CH ₄ (%)	CO (%)	CO ₂ (%)	C ₂ H ₂ (%)	C ₂ H ₄ (%)	C ₂ H ₆ (%)	C ₃ H ₆ (%)	C ₃ H ₈ (%)	C ₄ H ₈ (%) (iso)	C ₄ H ₈ (%) (n)	C ₄ H ₁₀ (%) (iso)	C ₄ H ₁₀ (%) (n)	C ₅ H ₁₀ (%) (iso)	C ₅ H ₁₀ (%) (n)	C ₅ H ₁₂ (%) (iso)	C ₅ H ₁₂ (%) (n)
Brine solution																		
1	300	0	1.42	0	6.23	25.17	8.24	13.7	17.41	2	8.98	2.87	4.87	1.82	2.29	2.29	1.01	1.69
	350	0.76	29.57	0.2	15.62	14.68	4.8	7.99	10.15	1.17	5.24	1.67	2.84	1.06	1.33	1.34	0.59	0.99
	400	0.33	29.3	0.03	8.38	13.29	3.68	10.34	8.17	5.1	5.5	1.84	3.75	3.44	4.34	0.84	0.83	0.82
2	300	0	5.37	0	7.6	23.72	7.76	12.91	16.4	1.89	8.46	2.71	4.59	1.71	2.16	2.16	0.96	1.6
	350	0.78	31.77	0.19	11.89	14.4	7.47	10.59	7.19	1.15	5.07	1.62	2.75	1.03	1.29	1.29	0.57	0.96
	400	0.32	29.7	0.03	5.3	12.68	7.02	9.86	7.79	4.92	5.76	1.93	3.93	3.6	4.54	0.88	0.87	0.86
3	300	0	6.34	0	8.76	23.14	7.57	12.6	16	1.84	8.26	2.64	4.48	1.67	2.1	2.1	0.93	1.56
	350	0.71	31.77	0.19	12.81	14.18	7.35	10.43	7.08	1.13	4.99	1.6	2.71	1.01	1.27	1.27	0.56	0.94
	400	0.3	28.73	0.03	5.34	12.47	6.9	9.69	7.66	4.83	6.19	2.07	4.22	3.87	4.88	0.95	0.93	0.92
4	300	0	8.61	0	9.14	22.42	7.34	12.2	15.5	1.78	8	2.56	4.34	1.62	2.04	2.04	0.9	1.51
	350	0.65	32.2	0.18	10.17	14.77	7.66	10.86	7.37	1.17	5.2	1.66	2.82	1.05	1.33	1.33	0.59	0.98
	400	0.22	29.48	0.03	3.44	12.39	6.86	9.63	7.61	4.8	6.57	2.2	4.48	4.11	5.18	1.01	0.99	0.98

DI water																		
1	300	0.00	0.20	0.00	8.66	25.43	8.32	13.84	17.58	2.02	8.32	2.66	4.52	1.68	2.12	2.12	0.94	1.57
	350	0.36	31.00	0.21	13.30	15.38	5.03	8.37	10.64	1.22	5.04	1.61	2.73	1.02	1.28	1.28	0.57	0.95
	400	0.20	28.87	0.03	11.10	13.09	3.63	10.18	8.05	5.03	5.10	1.71	3.48	3.19	4.02	0.78	0.77	0.76
2	300	0.00	5.37	0.00	7.60	23.72	7.76	12.91	16.40	1.89	8.46	2.71	4.59	1.71	2.16	2.16	0.96	1.60
	350	0.30	39.67	0.19	14.52	11.54	4.67	7.76	7.13	1.14	4.51	1.44	2.45	0.91	1.15	1.15	0.51	0.85
	400	0.18	24.45	0.03	12.32	12.68	7.02	9.86	7.80	4.86	5.35	1.79	3.65	3.35	4.22	0.82	0.81	0.80
3	300	0.00	7.07	0.00	9.77	22.67	7.42	12.34	15.68	1.80	8.09	2.58	4.39	1.64	2.06	2.06	0.91	1.53
	350	0.46	39.20	0.19	15.46	11.41	4.61	7.68	7.05	1.12	4.46	1.43	2.42	0.90	1.14	1.14	0.50	0.84
	400	0.24	22.37	0.03	13.38	12.49	6.92	9.72	7.68	4.78	5.76	1.93	3.93	3.61	4.54	0.88	0.87	0.86
4	300	0.00	9.57	0.00	10.15	21.88	7.16	11.91	15.13	1.74	7.81	2.50	4.24	1.58	1.99	1.99	0.88	1.47
	350	0.44	38.32	0.18	13.08	12.25	4.95	8.24	7.56	1.20	4.79	1.53	2.60	0.97	1.22	1.22	0.54	0.90
	400	0.22	21.43	0.03	14.17	12.24	6.78	9.52	7.52	4.69	6.03	2.02	4.11	3.77	4.75	0.92	0.91	0.90

Table 5.5. Relative concentration of hydrocarbon and permanent gases obtained from hydrous pyrolysis in brine solution and DI water separately at isothermal pyrolysis temperature of 300°C, 350°C, and 400°C.

Temp (°C)	H ₂ (%)	CH ₄ (%)	CO (%)	CO ₂ (%)	C ₂ H ₂ (%)	C ₂ H ₄ (%)	C ₂ H ₆ (%)	C ₃ H ₆ (%)	C ₃ H ₈ (%)	C ₄ H ₈ (%) (iso)	C ₄ H ₈ (%) (n)	C ₄ H ₁₀ (%) (iso)	C ₄ H ₁₀ (%) (n)	C ₅ H ₁₀ (%) (iso)	C ₅ H ₁₀ (%) (n)	C ₅ H ₁₂ (%) (iso)	C ₅ H ₁₂ (%) (n)
Brine solution																	
300	0.00	4.85	0.00	6.87	21.44	7.02	11.67	14.82	1.71	7.65	2.44	4.15	1.55	3.02	3.02	4.07	5.72
350	1.28	27.97	0.17	10.47	12.68	6.57	9.32	6.33	1.01	4.46	1.43	2.42	1.47	2.45	3.61	3.90	4.47
400	0.43	26.18	0.03	4.86	11.36	6.29	8.83	6.98	4.41	5.64	1.89	3.85	3.53	4.51	3.19	3.23	4.79
DI water																	
300	0.00	5.37	0.00	7.60	23.72	7.76	12.91	16.40	1.89	8.46	2.71	4.59	1.71	2.16	2.16	0.96	1.60
350	1.40	25.22	0.15	7.61	9.23	5.73	6.21	5.70	2.91	3.61	1.15	1.96	4.98	5.17	5.17	6.78	7.05
400	0.74	20.33	0.03	5.24	10.55	5.84	8.20	6.48	4.04	4.45	3.49	3.04	1.78	3.51	5.56	6.55	7.17

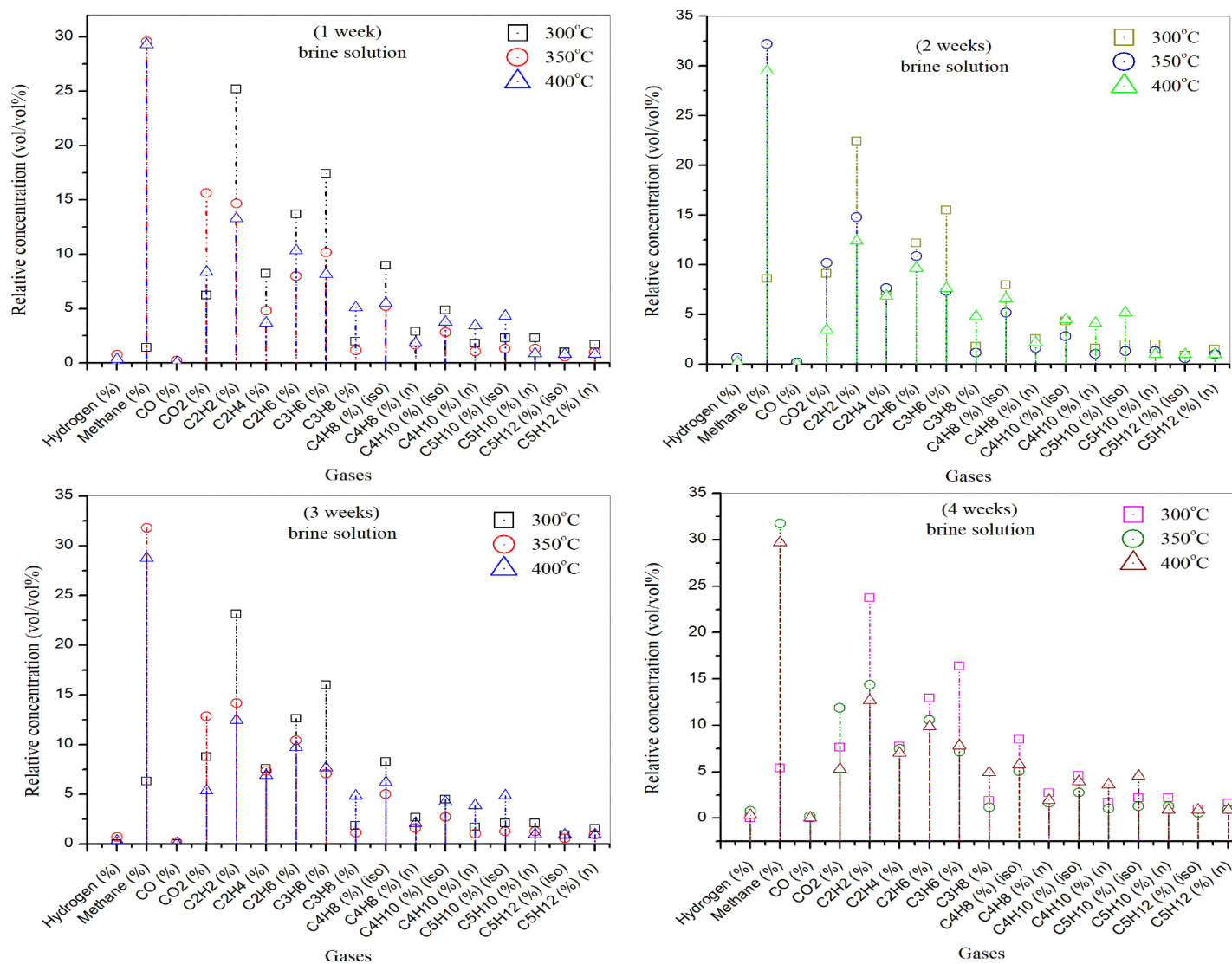


Fig 5.3. Relative concentration of permanent and hydrocarbon gases obtained from soaking pyrolysis experiments in brine solution.

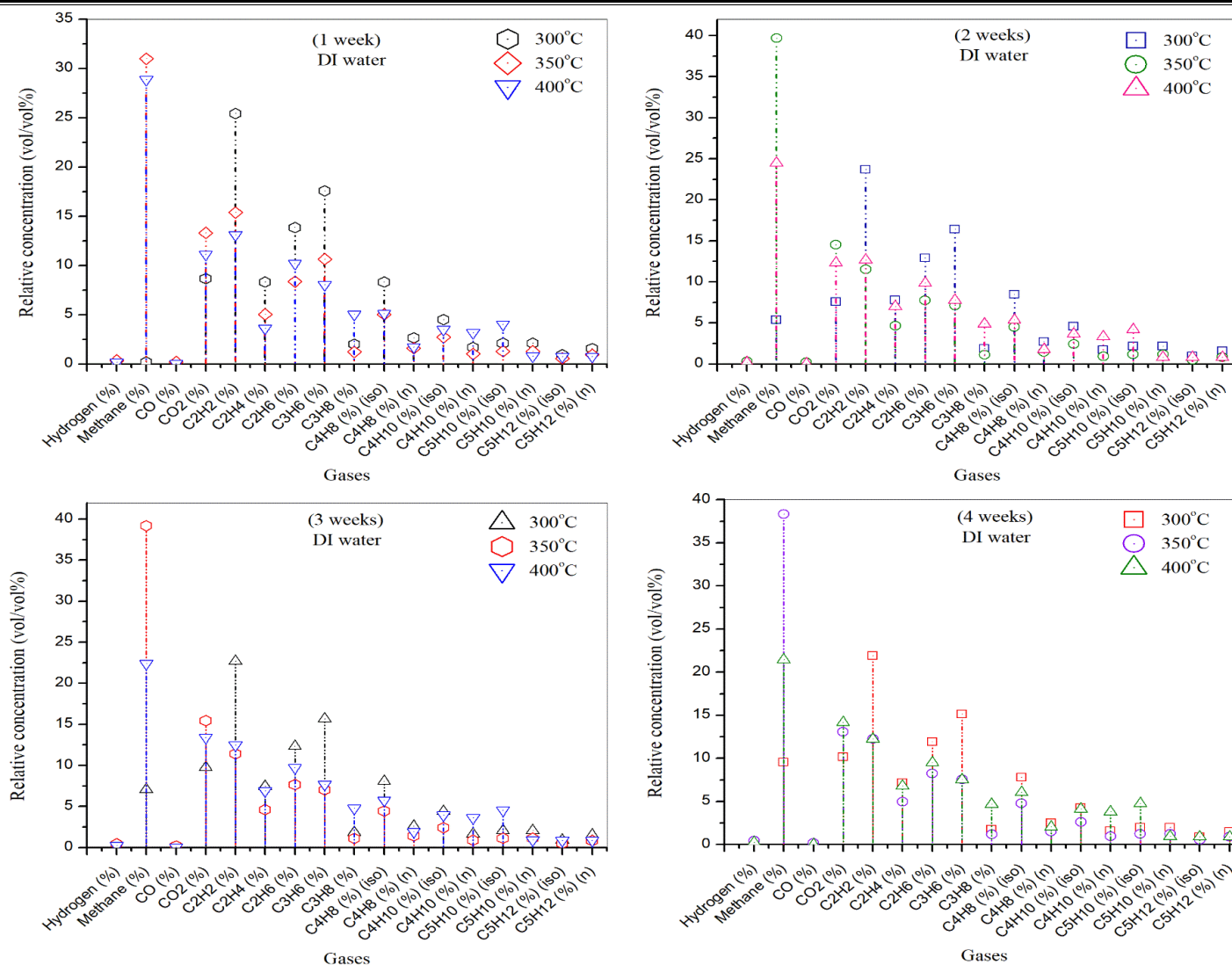


Fig 5.4. Relative concentration of permanent and hydrocarbon gases obtained from soaking pyrolysis experiments in DI water.

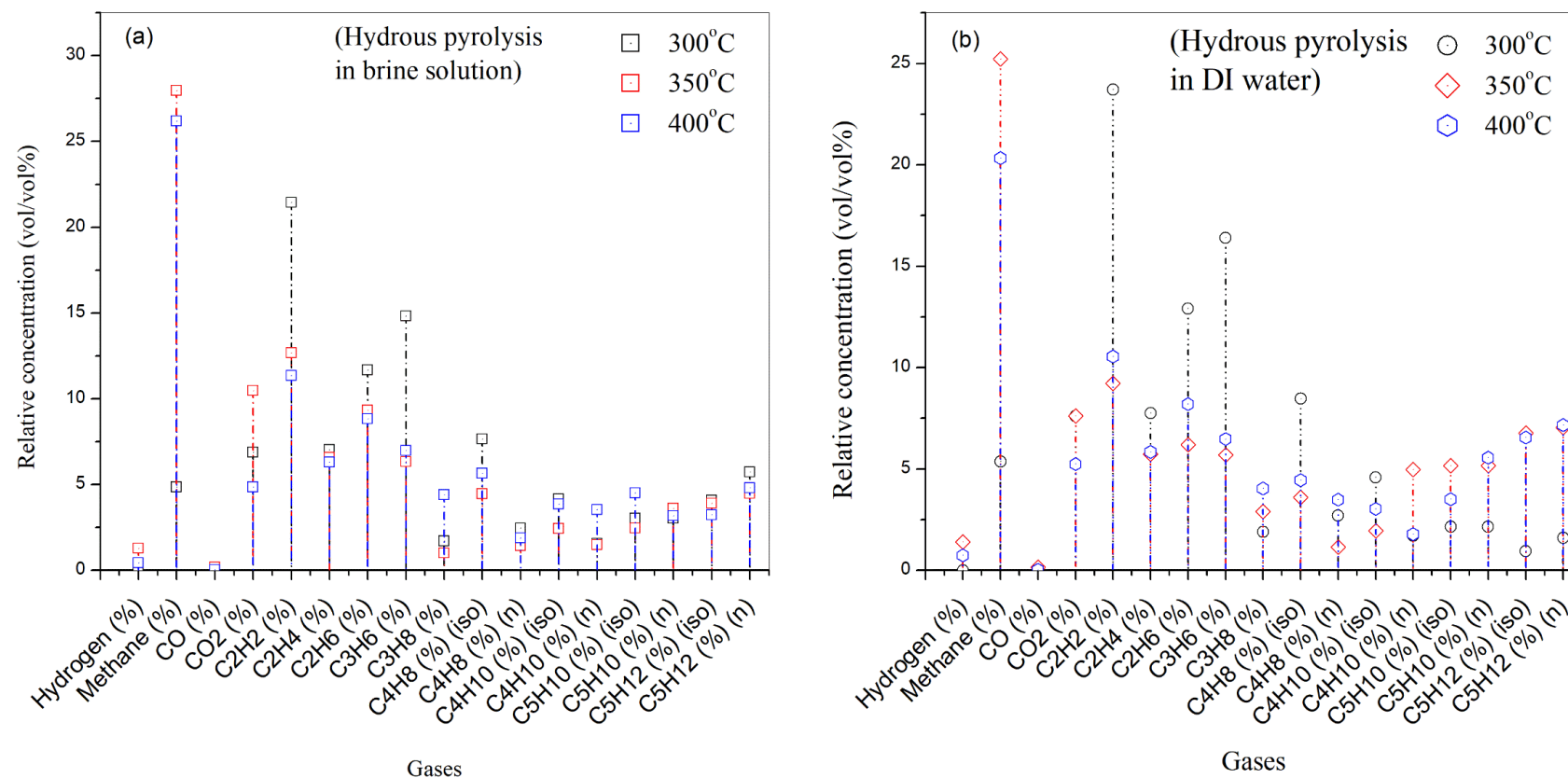


Fig 5.5. Relative concentration of permanent and hydrocarbon gases obtained from hydrous pyrolysis experiments in brine solution and DI water.

5.2.2. FTIR analysis of oil and water samples

The FTIR spectra of the oil samples obtained by soaking pyrolysis of oil shale samples in brine solutions and DI water are shown in Fig 5.6 (a) and (b). The FTIR spectra of the oil samples obtained from hydrous pyrolysis experiments are presented in Fig 5.6 (c), with the FTIR spectra of the formation water in Fig 5.6 (d). The assignment of wavenumbers of the identified functional groups for each oil sample and their relative percentage is tabulated in Tables 5.6 and Table 5.7. FTIR-ATR analysis showed that the oil samples obtained from soaking pyrolysis experiments using DI water for 1 to 4 weeks showed a broad band corresponding to aliphatic compounds from 2500 to 3000 cm^{-1} with a sharp peak at 2950 cm^{-1} . A small band corresponding to aromatic compounds ($\text{C}=\text{C}$) was observed from 1300 to 1480 cm^{-1} and a sharp peak at 680 cm^{-1} . A sharp peak of phenolic compounds was observed at 1150 cm^{-1} for the oil obtained from the sample with a soaking time of 1 week. However, the intensity of the peak decreased gradually for the oils obtained from 2, 3, and 4 weeks of soaking time. The oil samples obtained from soaking pyrolysis in brine solution also showed the high intensity of the aliphatic group occurring from 2500 to 3000 cm^{-1} with a sharp peak at 2950 cm^{-1} . A sharp peak corresponding to aromatics was observed from 1450 to 1500 cm^{-1} for the oil obtained from 1-week soaking, and two sharp peaks at 1450 and 1500 cm^{-1} for oil obtained from soaking periods of 2, 3, and 4 weeks.

All the oil samples showed a high intensity of phenolic compounds with the occurrence of a sharp peak at 1150 cm^{-1} . The oil sample obtained from hydrous pyrolysis experiments at 400°C in the presence of DI water showed the presence of aliphatic compounds with a wide band occurring from 2500 to 2950 cm^{-1} and aromatic compounds from 1390 to 1450 cm^{-1} and a sharp peak of small intensity at 680 cm^{-1} . The oil obtained from the hydrous pyrolysis experiment in brine solution at 400°C showed an abundance of aliphatics (2500 to 2950 cm^{-1}) and phenolic compounds (1150 cm^{-1}) with a small percentage of aromatics (680 cm^{-1} and 1490 cm^{-1}). The

water sample extracted from the hydrous pyrolysis experiments showed a broad peak corresponding to -OH group from 3000 cm^{-1} to 3500 cm^{-1} . A sharp peak showing the presence of -C=O, -COO- stretch and C=C aromatic compounds was observed to occur at 1600 cm^{-1} . The aromatic compounds may have occurred due to a small percentage of dissolved oil present in the water sample after separating the produced pyrolytic oil. The aqueous phase produced from soaking pyrolysis and the residual water collected after hydrous pyrolysis were analyzed to evaluate the presence of organic acids and dissolved hydrocarbons. All the water samples showed similar composition with OH from -COOH and -COH, with a traceable amount of aromatic C=C, -C=O stretch, and -COO- stretch. The aromatics may have occurred in the water sample due to dissolved hydrocarbons present in the water and the aqueous phases, as it is difficult to separate the hydrocarbons entirely from the water[72].

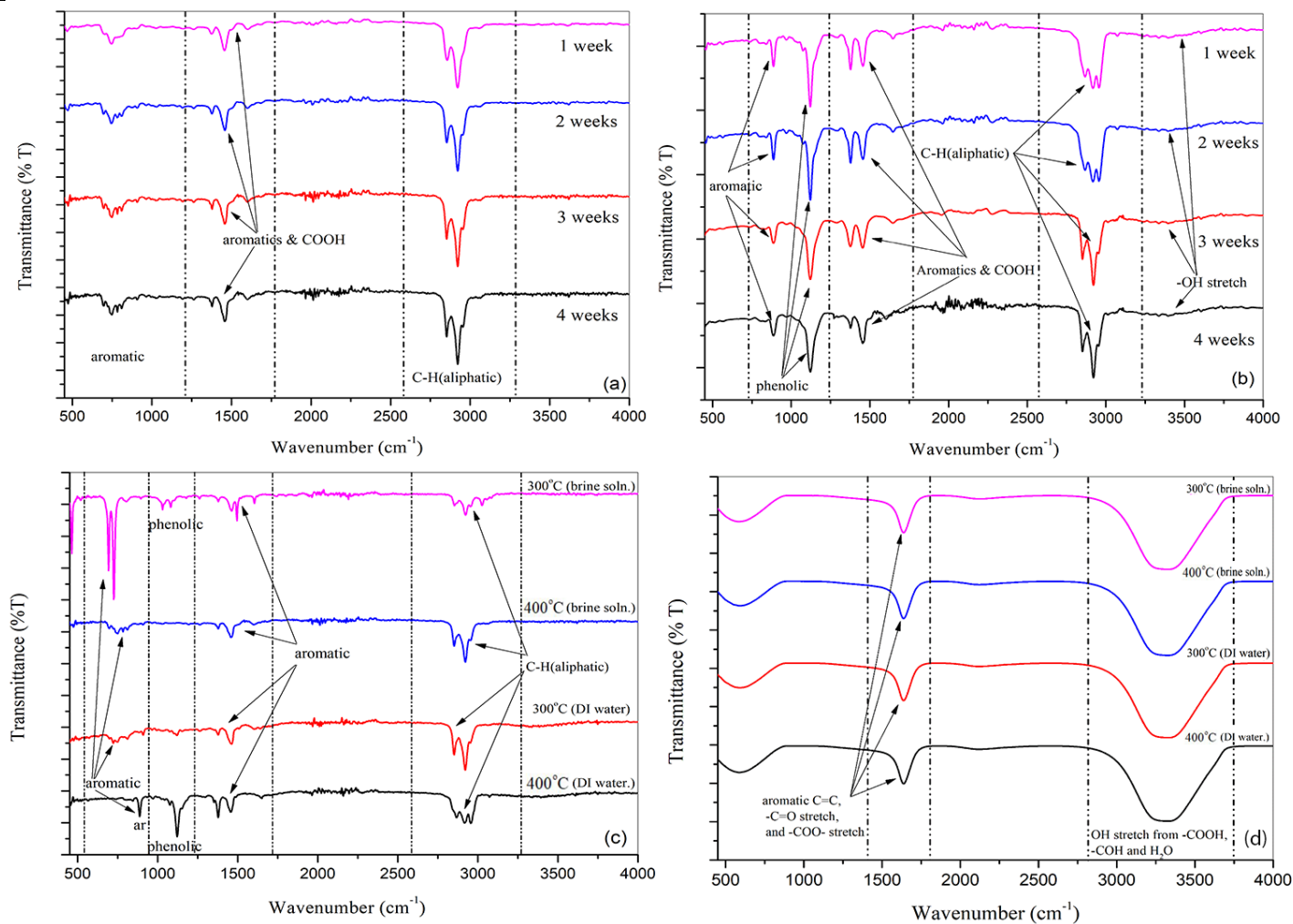


Fig 5.6. FTIR spectra of oil produced from soaking pyrolysis experiments in (a) brine solution, (b) DI water, (c) hydrous pyrolysis in brine solution and DI water, and (d) formation water from hydrous pyrolysis experiments.

Table 5.6. Functional groups corresponding to different wavenumbers.

Wavenumbers(cm^{-1})	Functional Groups
3625	-OH group; Alcohols and Phenols (strong; sharp)
3300-3500	-OH stretch from $-\text{COOH}$ and $-\text{COH}$
3000-2500	C-H stretch; Alkanes
1600-1650	Aromatics (Phenolic), $-\text{C}=\text{O}$ vibration; - C=O stretch from H-bonded conjugate
1400-1600	Aromatics
860-680	Aromatic C-H Stretch;
680-610	S-O bending; sulfates

Table 5.7. Relative concentration of identified functional groups for oil samples obtained from soaking and hydrous pyrolysis experiments in brine solution and DI water, and comparison with anhydrous pyrolysis.

Wavenumber (cm ⁻¹)	Functional Groups	Soaking pyrolysis								Hydrous pyrolysis		
		Brine solution				DI water				DI water	Brine solution	Anhydrous pyrolysis [22]
		1 week	2 weeks	3 weeks	4 weeks	1 week	2 weeks	3 weeks	4 weeks			
3000	CH (aliphatic)	47.31±0.20	52.75±0.15	58.11±0.05	31.06±0.19	37.52±0.10	35.80±0.21	39.30±0.28	42.04±0.27	38.24±0.30	38.32±0.24	32.4±1.1
3300	-OH	0	0	0	0	16.16±0.18	15.58±0.56	12.72±0.07	10.05±0.17	10.16±0.15	15.39±0.05	14.6±1.3
1600	C=O	23.73±0.12	7.44±0.10	0	18.05±0.07	4.34±0.21	5.16±0.31	5.67±0.43	5.19±0.50	5.55±0.25	3.61±0.10	11.5±0.7
1458	Aromatics	18.60±0.07	15.03±0.08	21.64±0.07	10.57±0.10	14.64±0.25	16.08±0.54	15.70±0.08	16.30±0.35	17.1±0.35	14.72±0.21	12.6±0.5
1000-1200	Phenolic, ether and alcohol	4.09±0.15	7.23±0.05	0	0	21.21±0.32	21.44±0.15	20.09±0.15	20.75±0.36	23±0.45	22.36±0.15	16.7±1.3
600-800	Aromatics	6.25±0.22	17.53±0.15	20.24±0.05	40.29±0.45	6.08±0.41	5.91±0.54	6.33±0.21	5.73±0.41	5.92±0.51	5.57±0.12	12±1.9

5.2.3. GC-MS analysis of oil samples

GC-MS analysis of the pyrolytic oils obtained from soaking and hydrous pyrolysis experiments in brine solution and DI water showed the presence of compounds in the range of C_6 to C_{38} . The GC spectra of the GC-MS analysis for each oil sample obtained from soaking pyrolysis (4 weeks) and hydrous pyrolysis experiments in brine solution and DI water at 400°C are shown in Fig 5.7 (a-d). The GC spectra for soaking time of 1 to 3 weeks in both DI water and brine solution separately are presented in Fig 5.8 (a-f). The compounds identified from GC-MS analysis are tabulated in Table 5.8, and the relative quantification of the identified compounds based on their functional group is presented in Table 5.9. The oil samples obtained from Soaking and hydrous pyrolysis experiments in brine solution and DI water showed the presence of compounds of molecular weight from 86 mol/g to 376 mol/g, as compared to the oil obtained from anhydrous pyrolysis, which showed the presence of compounds from 92 to 376 mol/g (Table 5.8). Previous studies on anhydrous pyrolysis showed the presence of 50.29% aliphatics, 20.66% aromatics, 8% phenolic, 2.07% sulfur compounds, and 18.72% organic acids and other heteroatomic compounds[22]. In the present study, the oil samples obtained from soaking pyrolysis experiments from week 1 to 4 in brine solution were found to be abundant in aliphatic content (46.47%, 49.13%, 43.30%, and 42.35%, respectively), with 22%, 24%, 27%, and 25% of aromatics, with 11%, 14%, 14%, and 17% of phenolic compounds, and with 15%, 13%, 17%, and 12% of organic acids. The concentration of amides ranged from 0.9% to 1.23% and followed an inverted-bell trend with an increase in soaking time (Table 5.9). The sulfur moieties were attached to the aliphatic chains and aromatic rings and ranged from 2.8 % to 2.5%. Oil samples obtained from soaking pyrolysis in DI water showed 42%, 40%, 41%, and 42.8% aliphatics for soaking times of 1, 2, 3, and 4 weeks. The aromatic concentration decreased with an increase in soaking time from 1 to 4 weeks and was recorded to be 17%, 21%, 21%, and 20%, respectively; however, the phenolic concentration increased with an

increase in soaking time as 12%, 15%, 19%, and 20%, respectively. Soaking pyrolysis in DI water showed a relatively higher concentration of organic acids with 25.3%, 20.65%, 17.8%, and 14% for oil samples of weeks 1, 2, 3, and 4, respectively. The concentration of amides was found to be fairly constant, ranging from 1.4% to 1%, with variation in soaking time. Also, the concentration of the sulfur moieties was lower in the presence of DI water compared to brine solution and ranged from 2.05% to 2.5% with a change in soaking time. However, no definitive trend was observed in the evolution of sulfur moieties with the variation in soaking time. The oil samples obtained at 400°C for hydrous pyrolysis experiments in brine solution and DI water showed 48% and 40.5% aliphatics, respectively, with 24% and 21% aromatics, 9% and 15% phenolics, and 28.9% and 22.5% organic acids. The production of oxygen-bearing compounds may have occurred due to the interaction between organic matter and water-oxygen species. This may lead to change in the oxygen isotope signatures of produced hydrocarbons by exchange leading to the formation of carboxylic acids or by addition leading to the formation of phenols[229]. The concentration of amides and sulfur moieties was similar in percentage to that during soaking pyrolysis in brine solution and DI water, respectively (Table 5.9). A high percentage of n-alkanes was also observed by Zhang et al. at 400°C for hydrous pyrolysis of Lucaogua Shale of China.[230] The high concentration of aliphatics in the oil samples may have occurred because n-alkanes are formed due to free radical reactions, and the branched iso-alkanes are formed due to carbonium ions reaction of α -olefins with protons[84]. Also, during hydrous pyrolysis, the aliphatic compounds of kerogen break down to generate n-alkanes and terminal n-alkenes by free radical hydrocarbon cracking. The produced n-alkenes simultaneously undergo reduction to form n-alkanes and oxidation to form ketones. The terminal n-alkenes also undergo rapid isomerization to form internal alkenes due to acid-catalyzed isomerization under hydro-thermal conditions by exchange of protons between water and produced hydrocarbons [83]. Eglinton et al. [231] observed ten folds increase in the

concentration of aliphatics with increase in pyrolysis temperature above 330°C. Also, the olefins in the gaseous state are unstable and readily hydrogenated into saturated hydrocarbons [84, 232]. The hydrogenation of olefins to n-alkanes occurs due to the presence of water, which acts as an excellent hydrogen donor in the presence of polar compounds and heteroatoms [83, 233]. The increase in the concentration of organic acids and heteroatoms with increase in soaking time may have occurred because during the peak stage of hydrocarbon generation the surrounding or absorbed water gets consumed [234] leading to generation of heteroatomic compounds. The concentration of organic acids produced during hydrous pyrolysis experiments were found to be in the good agreement with the values reported by Kharaka et al. [228]. The concentration of the aromatics and phenolic compounds was observed to be relatively higher than that of natural crude and oil produced from anhydrous pyrolysis of the oil shale sample. Eglinton et al. [231] and Rowland et al. [82] also reported similar findings. They reported increase in yield of aromatics with an increase in pyrolysis temperature during hydrous pyrolysis. They reported the aromatics to occur in the form of alkyl naphthalenes and alkylated sulfur (thiols) to aromatic ring. The increase in the percentage of aromatics was observed in our previous work to occur due to the aromatization of n-alkanes at elevated pressure and temperature [235]. The concentration of sulfur moieties in the oil samples from Soaking and hydrous pyrolysis appeared to be slightly higher than in oil obtained from previously reported [22] anhydrous pyrolysis (Table 5.9). The sulfur moieties were predominantly present in the form of thiophene sulfur. The trend of evolution of the sulfur compounds was similar to the findings reported by Bolin et al. [236].

The presence of asphaltenes in the pyrolytic oil samples from hydrous pyrolysis and natural crude oil samples has been reported extensively [221, 237, 238]. Asphaltenes may have occurred as a residual of the pyrobitumen fraction which is produced during the thermal

maturation of kerogen. The occurrence of asphaltene provides an idea about the coke formation properties of the particular oil sample[239].



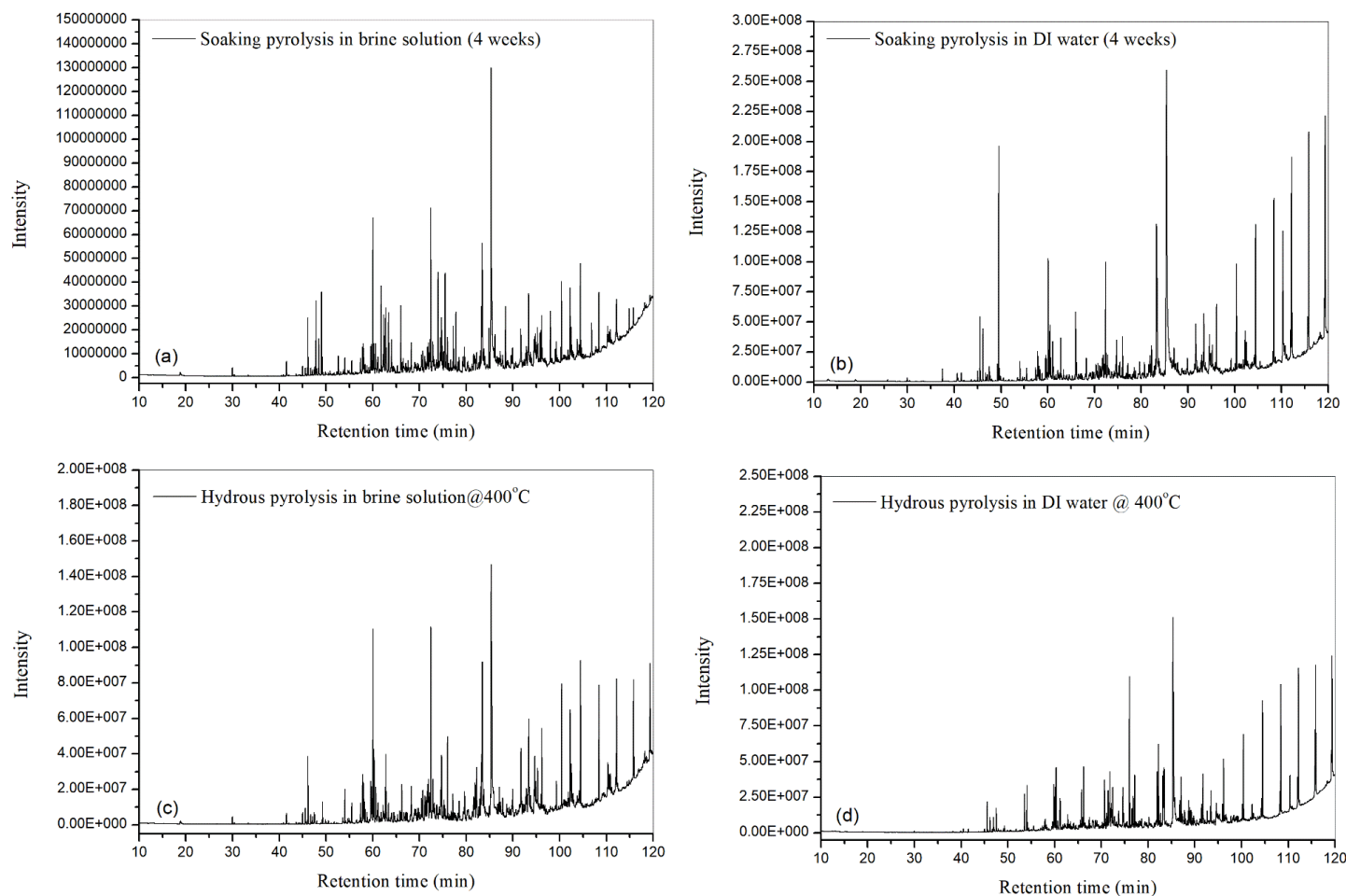


Fig 5.7. GC spectra of GC-MS analysis oil samples obtained from soaking pyrolysis in (a) brine solution, (b) DI water after a soaking period of 4 weeks, and hydrous pyrolysis in (c) brine solution, and (d) DI water at pyrolysis temperature of 400°C.

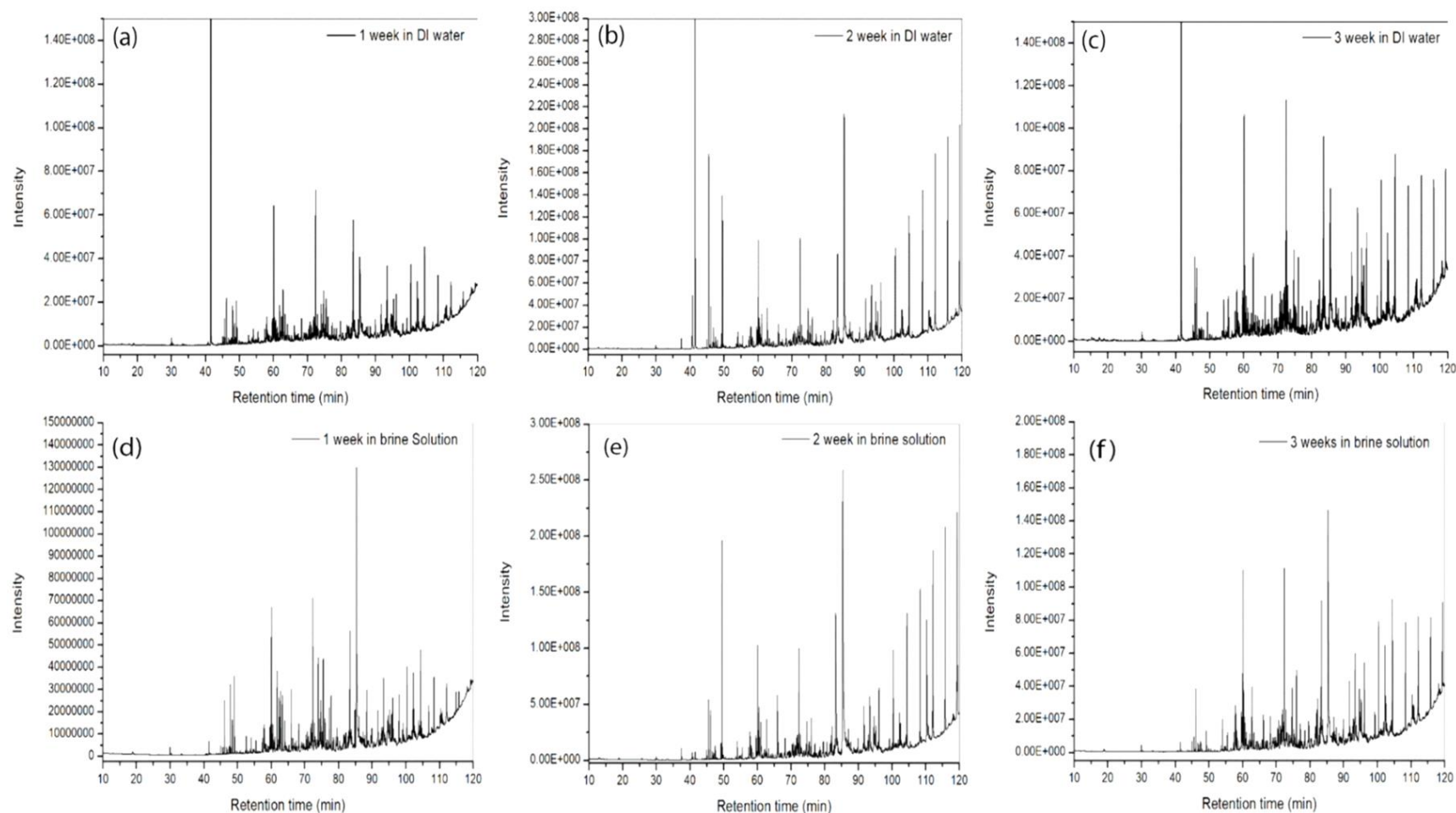


Fig 5.8. GC spectra of GC-MS analysis of oil samples obtained from soaking pyrolysis in DI water after a soaking period of (a) 1, (b) 2, and (c) 3 weeks, and hydrous pyrolysis in brine solution after soaking time of (d) 1, (e) 2, and (f) 3 weeks at pyrolysis temperature of 400°C.

Table 5.8. Quantification of different compounds identified using GC-MS analysis of oil sample from Soaking and hydrous pyrolysis in brine solution and DI water and comparison with anhydrous pyrolysis.

Sl. No.	Compound	Molecular Weight	Area %										
			Soaking pyrolysis								Hydrous pyrolysis		Anhydrous pyrolysis[2]
			Brine solution				DI water				Brine solution	DI water	
			Week 1	Week 2	Week 3	Week 4	Week 1	Week 2	Week 3	Week 4			
1	2-Methylpentane	86	0.44	0.76	0.23	0.77	0.82	0.72	0.99	1.66	1.44	1.76	---
2	p-xylene	106	0.53	0.69	0.78	0.83	0.75	0.67	0.83	0.82	0.82	0.91	0.61
3	Phenol	94	0.94	1.23	1.38	1.48	1.33	1.19	1.47	1.45	1.46	1.61	1.083
4	Phenol, 2-methyl-	108	1.42	1.85	2.07	2.23	2.00	1.79	2.21	2.18	2.20	2.42	1.63
5	Phenol, 3, 4-dimethyl-	122	3.30	4.29	4.82	5.19	4.65	4.17	5.14	5.08	5.12	5.63	3.79
6	Napthalene	128	1.25	1.63	1.83	1.97	1.77	1.58	1.95	1.93	1.95	2.14	1.44
7	Pentane, 3-Ethyl, 2,4-dimethyl	128	1.77	1.94	2.05	2.11	1.04	1.77	1.66	2.12	2.66	2.75	---
8	7-tetradecane	196	0.57	0.75	0.84	0.90	0.81	0.73	0.90	0.88	0.89	0.98	0.66
9	2-butyloctanol	186	1.11	1.44	1.62	1.74	1.56	1.40	1.72	1.70	1.72	1.89	1.27
10	1-Methyl-3-propylebenzene	134	---	---	1.77	2.05	---	0.77	0.81	1.69	2.12	2.55	---
11	Phenol, 2,3,6-trimethyl-	136	1.65	2.14	2.40	2.59	2.32	2.08	2.56	2.53	2.55	2.81	1.89

12	2-(2-hydroxyphenyl)buta, 1,3-diene	146	0.80	1.04	1.17	1.26	1.13	1.01	1.25	1.23	1.24	1.37	0.92
13	Indine, 1-ethylindene	141	1.65	2.14	2.40	2.59	2.32	2.08	2.56	2.53	2.55	2.81	1.89
14	Benzocycloheptatetra iene	142	1.74	2.26	2.54	2.74	2.46	2.20	2.71	2.68	2.70	2.97	2.00
15	2,2-Dimethyl,-3-heptanone	142	1.05	1.21	1.11	1.18	1.55	1.72	2.02	2.77	2.61	3.01	---
16	10 – Heneicosane (c,t)	294	2.04	2.65	2.98	3.20	2.87	2.57	3.18	3.14	3.16	3.48	2.34
17	Cis-3 hexenyl isovelerate	184	0.35	0.55	0.76	0.12	0.8	1.1	1.4	1.18	0.62	1.63	---
18	2,3-Dimethylbenzene, 1,4-diamine	136	0.22	0.25	0.18	0.11	0.41	0.7	0.11	0.76	0.55	0.32	---
19	4-methyldocosane	324	1.19	1.55	1.74	1.88	1.68	1.51	1.86	1.84	1.85	2.03	1.37
20	1-Nonadecane	266	0.78	1.01	1.13	1.22	1.09	0.98	1.21	1.19	1.20	1.32	0.89
21	1-Docosene	308	1.04	1.35	1.51	1.63	1.46	1.31	1.61	1.60	1.61	1.77	1.19
22	1-Methylnonadecane	282	0.96	1.25	1.40	1.51	1.35	1.21	1.49	1.47	1.49	1.63	1.10
23	Dodecane, 2,6,10-trimethyl-	212	1.85	2.40	2.70	2.90	2.60	2.33	2.88	2.84	2.87	3.15	2.12
24	1,12-Dodecanediamine	200	0.72	0.61	0.44	0.35	0.55	0.39	0.27	0.25	0.79	0.82	---
25	3-Buten-2-ol, 2,3, dimethyl-	100.16	1.55	0.44	0.73	1.38	0.33	1.21	1.18	1.69	1.20	1.89	1.74

26	9-Nonadecane	266	2.13	2.77	3.12	3.35	3.01	2.69	3.32	3.28	3.31	3.64	2.45
27	Nonadecane	268	1.17	1.52	1.70	1.83	1.65	1.47	1.82	1.80	1.81	1.99	1.34
28	Cyclohexane, 1,1'(2-methyl-1,3-propanediyl)-bis	222.4	1.12	1.57	1.81	1.32	1.06	1.45	1.88	2.57	2.61	3.71	2.77
29	Anthracene, 2-methyl-	192	1.28	1.66	1.87	2.01	1.80	1.62	1.99	1.97	1.99	2.18	1.47
30	1-Tricosene	322	0.95	1.23	1.39	1.49	1.34	1.20	1.48	1.46	1.47	1.62	1.09
31	10-methylnonadecane	282	1.18	1.54	1.73	1.86	1.67	1.50	1.85	1.82	1.84	2.02	1.36
32	Cyclohexyl 2,2-dimethylpentanoate	170	1.44	1.29	1.57	2.10	1.87	1.99	1.87	2.05	2.32	2.44	2.08
33	1-Phenylhexan-2-one	176.25	1.05	1.08	1.12	1.54	1.07	1.12	1.24	1.35	1.88	1.51	1.22
34	6-octadecanoicacid, methyl ester (Z)	296	1.32	1.72	1.93	2.08	1.87	1.67	2.06	2.04	2.05	2.26	1.52
35	1,1-di(4-methylcyclohexyl)do decane	362	1.70	2.21	2.48	2.67	2.39	2.14	2.65	2.61	2.64	2.90	1.95
36	Heptadecane, 9-hexyl-	322	1.17	1.52	1.70	1.83	1.65	1.47	1.82	1.80	1.81	1.99	1.34
37	Heptadecane	240	2.58	3.35	3.76	4.05	3.63	3.25	4.02	3.97	4.00	4.40	2.96
38	1-Decanol, 2-hexyl-	242	1.39	1.81	2.03	2.19	1.96	1.76	2.17	2.14	2.16	2.38	1.60
39	1,2,4-Benzenetricarboxylic	294.3	1.44	1.65	1.87	2.01	0.95	1.14	1.57	1.98	1.26	1.75	

	acid, 4 butyl, 1,2-dimethyl ester												---
40	Heptacosane	380	1.59	2.07	2.33	2.50	2.25	2.01	2.48	2.45	2.47	2.72	1.83
41	4-Methyldibenzothiophene	198.28	1.35	1.36	1.31	1.22	1.51	1.79	1.24	1.56	1.77	1.83	---
42	1-Dodecanol, 2-hyxl-	270	1.23	1.60	1.79	1.93	1.73	1.55	1.91	1.89	1.91	2.09	1.41
43	2-Methyltetracosane	352	1.32	1.71	1.92	2.07	1.85	1.66	2.05	2.02	2.04	2.24	1.51
44	Octadecanoicacid, 2-oxo-, methyl ester	312.48	1.76	1.88	2.10	2.34	2.56	1.01	1.26	1.49	2.01	2.52	---
45	1,3-Didecylbenzene	358.6	0.32	0.77	1.29	2.05	0.71	1.38	1.20	1.88	2.77	2.01	---
46	Isoquinoline	129.16	1.11	1.01	1.21	1.26	1.18	1.17	1.32	1.44	0.97	1.04	---
47	2-Ethyl dodecanol	214	1.64	2.13	2.39	2.57	2.31	2.07	2.55	2.52	2.54	2.79	1.88
48	Sulfurous Acid, hexyl pentadecyl ester	376	1.29	1.33	0.62	0.82	1.53	1.26	0.80	0.76	0.78	0.26	2.06
49	Hexadecane,1-(ethenyl oxy)	268	3.18	4.13	4.64	5.00	4.48	4.01	4.95	4.89	4.93	5.42	3.65
50	2-ethyl, 1-dodecanol	214	3.42	4.45	5.00	5.38	4.82	4.32	5.33	5.27	5.31	5.83	3.928

Table 5.9. Relative quantification of compounds based on GC-MS analysis for oil samples obtained from hydrous pyrolysis and soaking pyrolysis in brine solution and DI water for soaking time of 1 to 4 weeks at pyrolysis temperature of 400°C.

Classification of compounds	Brine solution				DI water				Brine solution	DI water	Anhydrous pyrolysis[22]
	1 week	2 weeks	3 weeks	4 weeks	1 week	2 weeks	3 weeks	4 weeks	400°C	400°C	
Aliphatics	46.47	49.13	43.30	42.35	42	40	41	42.8	48	40.5	50.29
Aromatics	22	24	27	25	17	21	21	20	24	21	20.66
Phenolics	11	14	14	17	12	15	16.5	20	9	15	8
Amides	1.23	1.17	0.9	1.15	1.3	1.4	1.2	1	0.9	1.05	---
Sulfur compounds	2.3	2.7	2.8	2.5	2.05	2.1	2.5	2.2	2.2	2.5	2.07
Organic acids	15	13	17	12	20.65	25.3	17.8	14	18.9	22.5	18.72

5.2.4. Simulated Distillation analysis of oil samples

Simulated distillation (SimDist) of the oil samples obtained from soaking and hydrous pyrolysis experiments were conducted to determine the carbon number distribution in the oil samples and identify the distillation fractions present. The pyrolytic oil obtained from soaking in brine solution for 1-4 weeks showed carbon number up to C_{38} (Fig 5.9 (a)) and oil obtained from soaking pyrolysis in DI water showed carbon number up to C_{34} (Fig 5.9 (b)). The oil produced from hydrous pyrolysis experiments in DI water and Brine solution showed carbon number distribution ranging from C_8 to C_{38} (Fig 5.9 (c)). The relative concentrations of the distillation fractions are summarized in Fig 5.10 (a-c). It was observed that the duration of soaking time did not affect the total carbon number distribution in the produced oil but changed the concentration of the distillation fractions. The pyrolytic oil produced after soaking for one week in brine solution showed 20% of light distillates, 24% middle distillates, and 56% of heavy distillates. The concentration of light distillates decreased to 18%, and the middle and heavy fractions increased to 26% and 53%, respectively. It was observed that for the oil obtained from soaking for 3 weeks, the concentration of heavy fractions decreased to 52%, with 24% middle and 22% light distillate fractions. However, for a soaking period of 4 weeks, the pyrolytic oil showed the presence of 57% heavy distillates, 18% light, and 25% middle distillates. Again, the oil obtained from 1 week of soaking in DI water showed the presence of 20% light distillates, 28% middle, and 52% heavy distillates. With an increase in soaking time, the concentration of heavy fractions decreased from 51% in oil obtained from soaking for two weeks to 47% and 46% in oil obtained from soaking for 3 and 4 weeks, respectively. The concentration of middle distillates increased from 33%, 37%, and 38%, respectively with an increase in soaking time from 2 to 4 weeks. The light fractions remained relatively constant throughout all the oil samples for soaking period of 2 to 4 weeks, showing a concentration of 16%. Although, it was observed that the oil sample obtained from the hydrous pyrolysis

experiments in brine solution also showed 56% of heavy fraction, with 23% middle distillates and 21% of light distillates. And the oil produced from standard pyrolysis experiments in DI water showed similar concentrations with 22% light distillates, 21% middle distillates, and 57% of heavy distillates. All the oil samples showed a noticeably higher concentration of heavy fractions. The occurrence of heavy distillation fraction denotes the presence of long-chain hydrocarbons. The presence of long-chain n-alkanes, and alkyl constituents of n-alcohol, n-ketone, n-ether, and n-acids in the oil produced from hydrous pyrolysis of oil shales was previously reported by Smith et al.[240]. The medium and long-chain distillates from C₈-C₃₀ are primarily formed by n-alkanes [230]. It was observed that the oil obtained from soaking pyrolysis in brine solution and standard pyrolysis in both brine solution and DI water showed a similar and nearly identical distribution of distillation fractions.

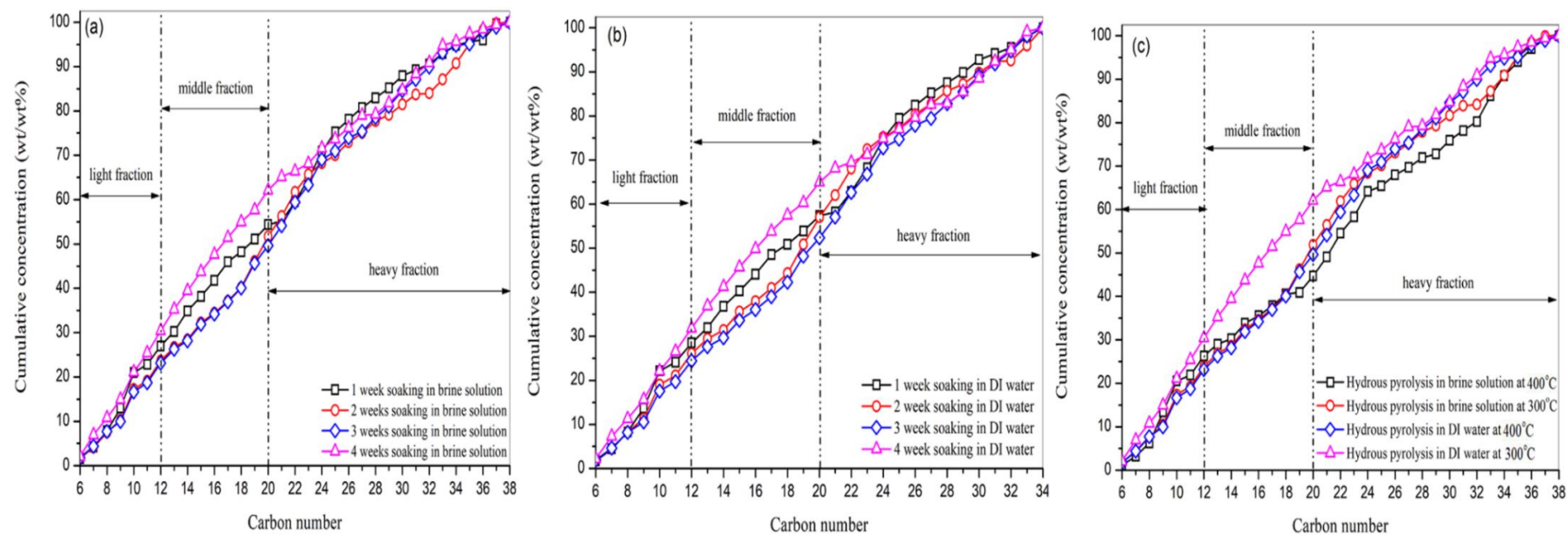


Fig 5.9. Simulated distillation curves of oil obtained from soaking pyrolysis at 400°C in (a) brine solution, (b) DI water, (c) hydrous pyrolysis in brine and DI water at 300 and 400°C.

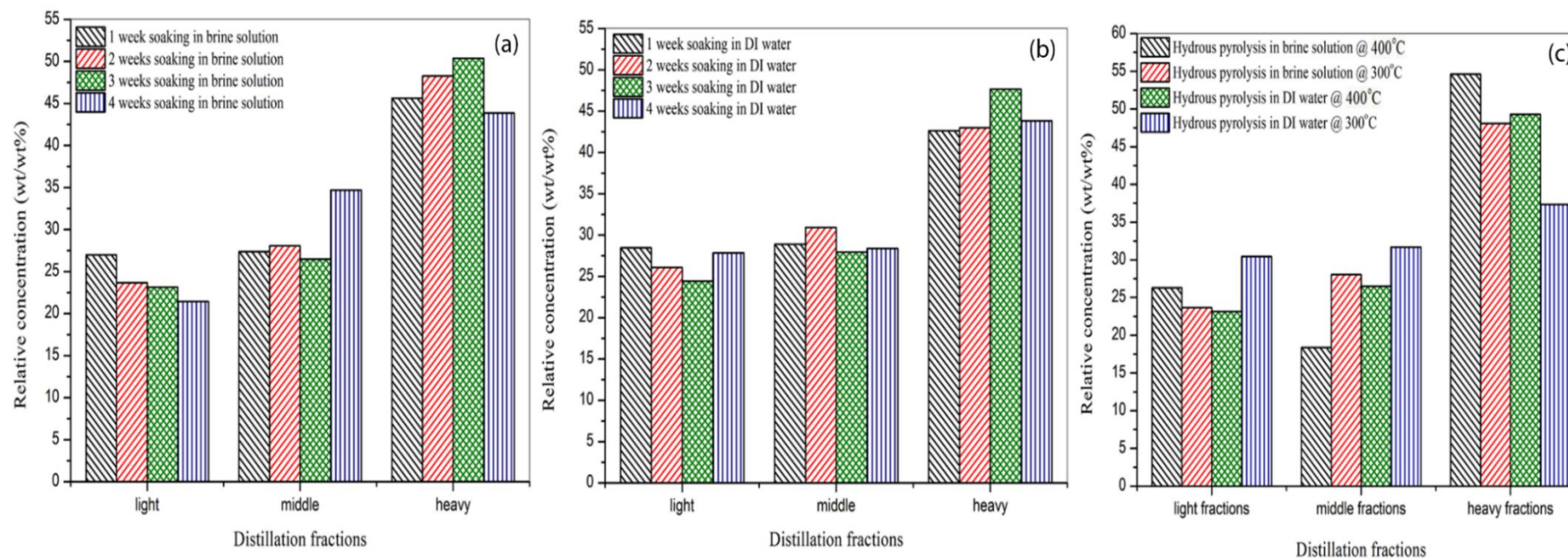


Fig 5.10. Relative distribution of distillation fractions in oil obtained from (d) brine solution, (e) DI water, and (f) from hydrous pyrolysis in brine and DI water.

5.2.5. ^1H NMR analysis of oil samples

The ^1H NMR spectra of the oil samples obtained from soaking pyrolysis for a soaking period of 4 weeks and hydrous pyrolysis in DI water and Brine solution at 400°C are shown in Fig 5.11 (a-d). The quantification of the identified functional groups of the oil samples are tabulated in Table 5.10. The NMR spectra of the oil samples obtained at 400°C for a soaking time of 1 to 3 weeks in both DI water and brine solution separately are presented in Fig 5.12 (a-f). The oil obtained from soaking pyrolysis experiments in DI water showed the occurrence of $-\text{OH}$ compounds and heteroatoms; however, the concentration of $-\text{OH}$ and heteroatoms were found in minute percentage in hydrous pyrolysis experiments. The presence of phenolic compounds was dominant in the oil samples obtained from both Soaking and hydrous pyrolysis. In the oil samples obtained from soaking in brine solution, the calculation of the integral area of different functional groups showed 44%, 42%, 46%, and 49% alkanes from 0-1.5 ppm for oil samples obtained from soaking in brine solution for 1, 2, 3 and 4 weeks, respectively. The concentration of aliphatic α -heteroatoms and unsaturation decreased from 18%, 18%, 19% and 18% with increase in soaking time from 1 to 4 weeks. The concentrations of α -methyl to aromatics were detected to be 15%, 17%, 11%, and 9% for soaking time from 1 to 4 weeks. 2% methoxy and carbohydrates were found in the oil sample obtained from 1-week soaking time. Nonetheless, the oil samples obtained from 2, 3, and 4 weeks of soaking time showed the absence of methoxy and carbohydrates. The concentration of aromatic compounds increased with an increase in soaking time. The concentration of aromatics was found to be 21%, 23%, 24%, and 24% for soaking times of 1, 2, 3, and 4 weeks respectively. It was observed that no ester or carboxylic acids were found in any of the oil samples obtained from soaking in brine solution. From soaking pyrolysis experiments in DI water, the concentration of aliphatics was found to be 41, 42, 40.3, and 42 % for soaking time from 1 week to 4 weeks. The concentration of aliphatic compounds was observed to be fairly constant for soaking times of 1 and 2 weeks and appeared

to decrease from weeks 3 to 4. The decrease in percentage of aliphatics can be compensated by the increase in concentration of the aliphatic α -heteroatoms or unsaturation from 28 to 38%. The concentration of α -methylene to aromatics increased from 4% in week 1 to 6.6% in week 3, and decreased to 5.1% in week 4 (Table 4). The concentration of aromatics was determined to be 17% in week 1, decreased to 14.8% in week 2, and remained fairly constant till week 4. The oil samples obtained from hydrous pyrolysis in brine solution showed 43% aliphatics followed by 41% in DI water. The concentration of aliphatic α -heteroatoms or unsaturation was found to be 17% and 18.5%, respectively. For hydrous pyrolysis in brine solution, the distribution of α -methylene to aromatics was calculated to be 11.2%, and for DI water, the concentration was calculated to be 10.1%. For the oil sample obtained from the hydrous pyrolysis in brine solution and DI water, the concentration of aromatics was identified to be 24.8% and 24.4%, respectively, followed by 4% and 6% ester and carboxylic acids. It may be noted that the distribution of aliphatics and aromatics for all the obtained oil samples were found to be similar to the percentage determined by GC-MS analysis. The total molecular weight of the oil samples produced from soaking pyrolysis in brine solution ranged from 1531 g/mol to 1586 g/mol. And, for the oil samples produced from Soaking pyrolysis in DI water, the total group molecular weight increased from 1517 g/mol to 1546 g/mol with increase in soaking time from 1 week to 4 weeks, respectively. For the oil samples produced from soaking pyrolysis in brine solution, the group molecular weight of aromatics increased from 316 g/mol to 385 g/mol with increase in soaking time from 1 week to 4 weeks. However, for the soaking experiments in DI water, the group molecular weight of aromatics decreased with increase in soaking time. Again, hydrous pyrolysis experiments in brine solution and DI water showed the total group molecular weight of 1561 g/mol and 1544 g/mol, and the group molecular weight of aromatics was 390 g/mol and 375.2 g/mol respectively. The oil samples obtained from the Soaking and hydrous pyrolysis experiments showed the total group molecular weight and

group molecular weight of aromatics to be slightly higher as compared to the oil sample obtained from anhydrous pyrolysis, which showed a total group molecular weight of 1489 g/mol and group molecular weight of aromatics as 335 g/mol[72]. The increase in total group molecular weights of the oil samples produced from Soaking and hydrous pyrolysis experiments may have increased due to a high percentage of aliphatic compounds and a higher concentration of heavy distillates from SimDist analysis in the present study. The increase in the group molecular weight of the aromatics compared to anhydrous pyrolysis is clearly due to the increase in the concentration of aromatics in the oil samples produced from Soaking and hydrous pyrolysis. The increase in the concentration of the aromatics in the presence of water has been previously reported to be due to the aromatization of aliphatic compounds[235].

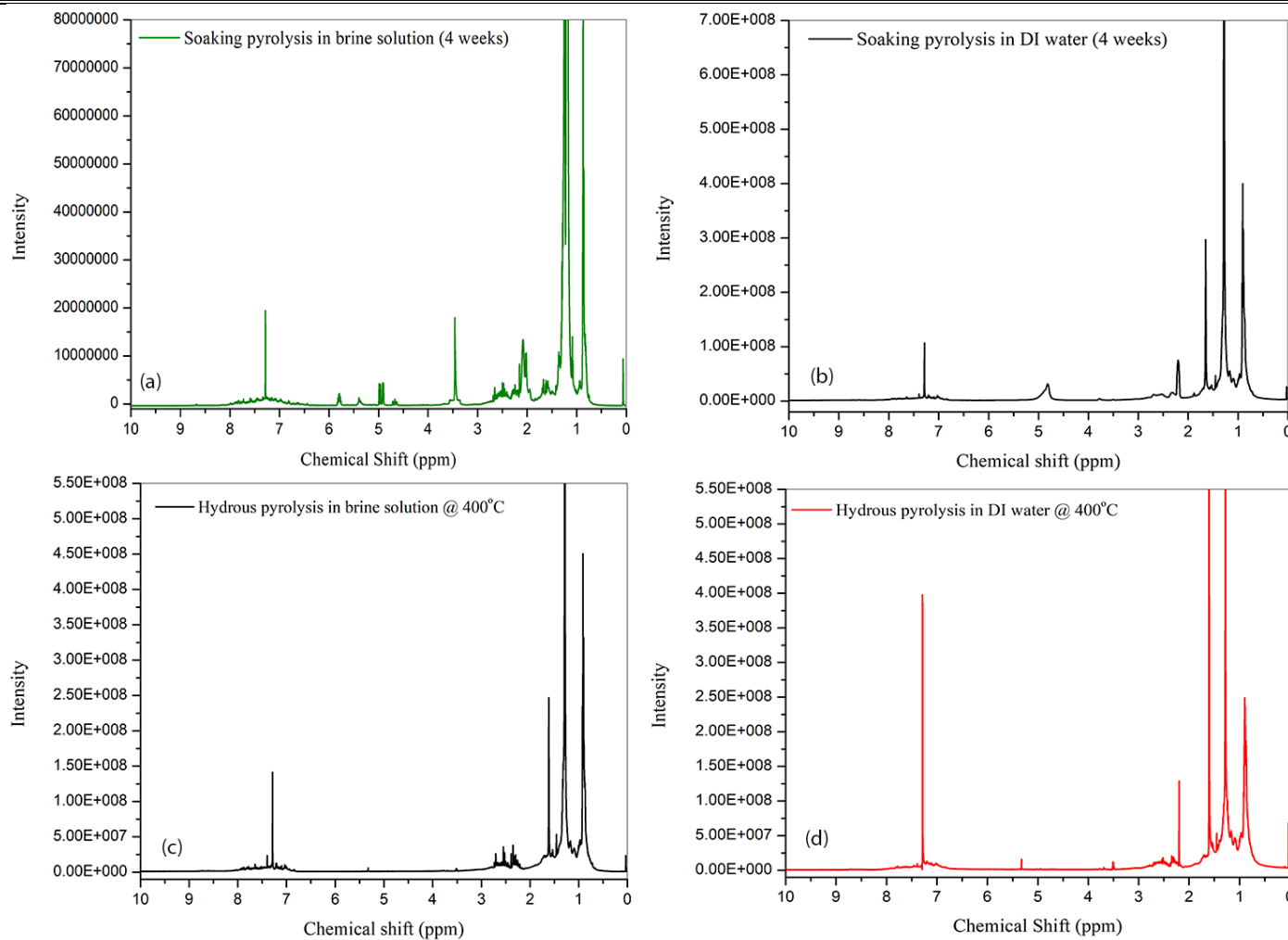


Fig 5.11. ^1H NMR spectra of oil produced by (a) soaking sample in brine solution, (b) DI water for soaking time of 4 weeks, (c) hydrous pyrolysis in brine solution and (d) DI water at 400°C.

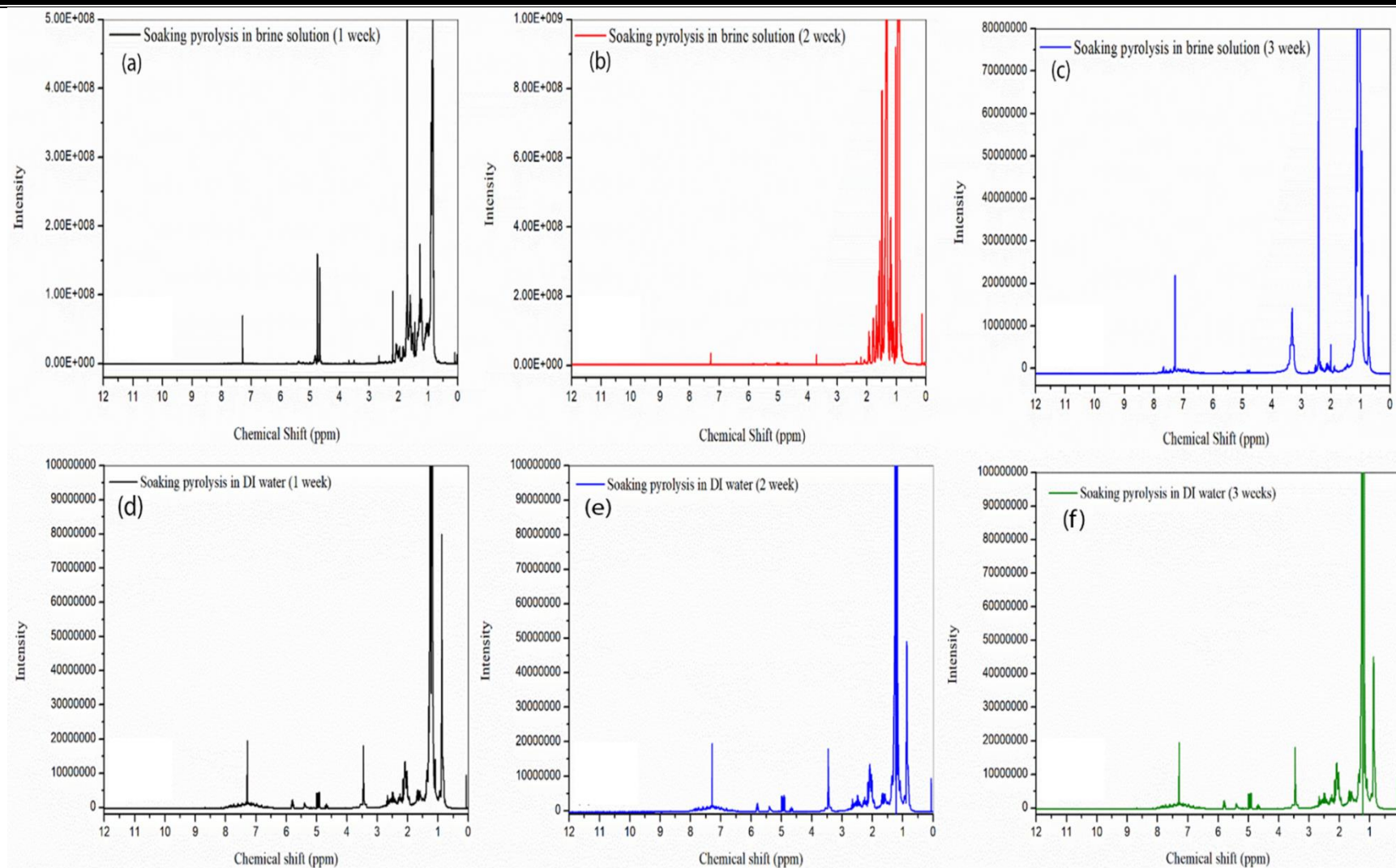


Figure 5.12. ^1H NMR spectra of oil produced by soaking pyrolysis in sample in brine solution for (a) 1 week, (b) 2 weeks, (c) 3 weeks and in brine solution for soaking time of (d) 1 week, (e) 2 weeks, and (f) 3 weeks in DI water at pyrolysis temperature of 400°C .

Table 5.10. Concentration of identified functional groups by ^1H NMR analysis from oil obtained from soaking pyrolysis in brine solution for 1, 2, 3 and 4 weeks.

Proton Assignment (¹ H)	Chemical Shift, ppm	Soaking pyrolysis experiments								Hydrous pyrolysis		Anhydrous pyrolysis[22, 72]	Upper Assam crude oil
		Brine solution				DI water							
		1 week	2 weeks	3 weeks	4 weeks	1 week	2 weeks	3 weeks	4 weeks	Brine	DI water		
Alkanes (%)	0.5-1.5	44±1.2	42±2	46±0.5	49±1	41±2	42±1	42.3±2	42±1	43±0.5	41±0	36±2	67.35±1
Aliphatics α-heteroatoms or unsaturations (%)	1.5-3	18±0.5	18±1.5	19±1	18±1.5	28±1	29±0	31.6±0.5	38.5±0.5	17±0	18.5±1	29±1	10.61±0.5
α-Methylene to aromatic (%)	3-4.5	15±1	17±2.5	11±0.5	9±0.5	4±3	4.2±1.5	6.6±0.5	5.1±0.5	11.2±1	10.1±0	10±1	11.21±1
Methoxys and carbohydrates (%)	4.5-6	2±1.7	0	0	0	0	0	0	0	0	0	3±0.5	2.40±2.5
Aromatic (%)	6-8.5	21±1.5	23±2	24±2	24±2.5	27±1	24.8±0.5	21.5±1	14.4±0	24.8±0	24.4±0.5	21±0.5	8.44±0
Esters and carboxylic acids (%)	8.5-10	0	0	0	0	0	0	0	0	4±0.5	6±0.45	1±0	0
Total group molecular weight of sample (g/mol)		1542±0.6	1531±0.5	1568±0.15	1586±0.2	1517±0.9	1524±1.5	1531±2.5	1546±1.5	1561±2.5	1544±2.5	1489±0.6	2361±1.2
Total group molecular weight of aromatic compounds (g/mol)		316±0.8	358.25±0.9	364.75±0.25	385±0.5	421±0.4	381±2.6	333±3	232.2±2.5	390±3	375.2±2	335±0.5	200.68±1

5.3. Conclusive summary

The Soaking and hydrous pyrolysis of Indian oil shale in the presence of DI water and brine solution showed the oil yield increases with pyrolysis temperature from 300°C to 400°C. GC analysis showed the gas samples to be abundant in CH₄. The concentration of C₂ to C₅ gases obtained from soaking pyrolysis decreased with increase in pyrolysis temperature. During hydrous pyrolysis, the concentrations of C₂ to C₃ gases decreased with increase in pyrolysis temperature. SimDist analysis of oil samples obtained from soaking pyrolysis showed carbon number distribution from C₆ to C₃₈ for brine solution and C₆ to C₃₄ for DI water. However, the oil samples obtained from hydrous pyrolysis experiments in brine solution and DI water at 400°C showed carbon number distribution from C₈ to C₃₈. GC-MS, ATR, and NMR analyses of the oil samples obtained during soaking pyrolysis at 400°C showed the concentration of organic acids to remain fairly constant in the presence of brine solution and an increasing-decreasing trend in the presence of DI water with increase in soaking time. The concentration of the organic acids obtained from hydrous pyrolysis appeared to be higher in the presence of DI water as compared to brine solution. The oil samples obtained from all the pyrolysis experiments were found to be aliphatic in nature. The concentration of alkanes increased with increase in soaking time. During hydrous pyrolysis the concentration of the aliphatics decreased with increase in pyrolysis temperature but remained fairly constant in the presence of DI water. The concentration of aromatic compounds obtained from soaking pyrolysis in brine solution increased with increase in soaking time, however, a reverse trend was observed in the presence of DI water. The concentration of the aromatic compounds in the oil sample obtained from hydrous pyrolysis remained fairly constant throughout all pyrolysis temperatures and water solutions. The yield of sulfur moieties was observed to be higher during hydrous and soaking pyrolysis experiments as compared to anhydrous. ¹H NMR

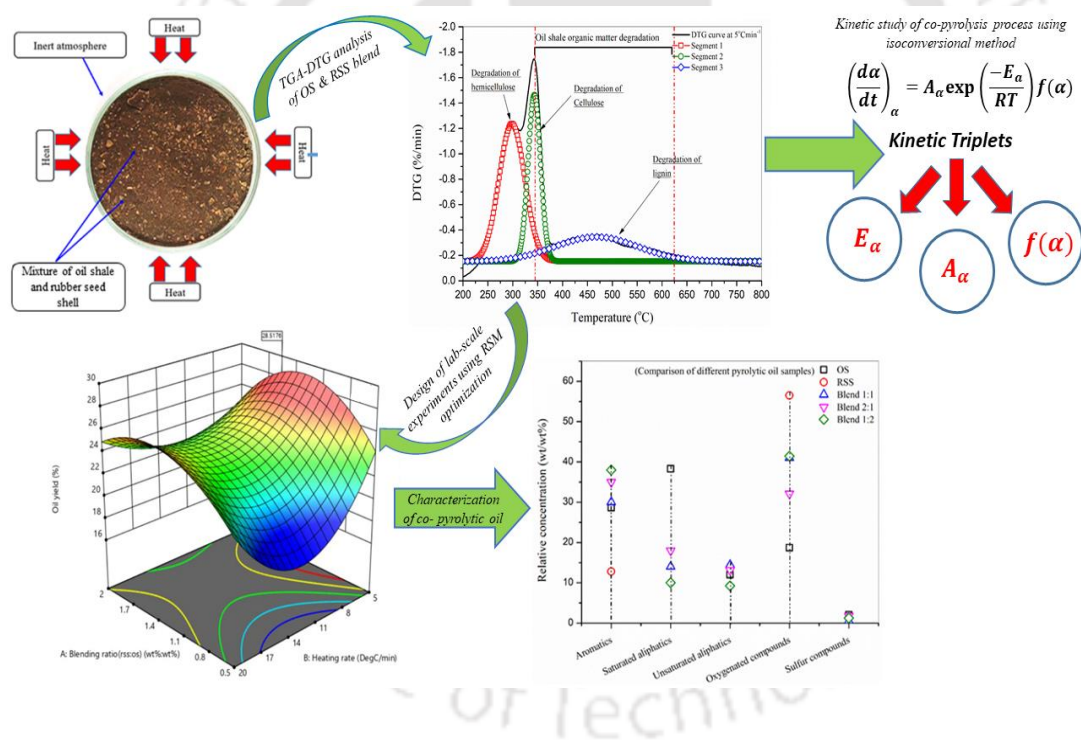
data revealed that the total group molecular weight of the oil samples obtained from both Soaking and hydrous pyrolysis appeared to be higher in the presence of brine solution as compared to DI water.



Chapter 6

Co-pyrolysis of oil shale and rubber seed shell; Product yield and optimization of parameters using RSM

- Co-pyrolysis
- Oil shale
- Rubber seed shell
- Kinetic study
- Optimization of process parameters
- Product characterization



Published as:

B. Baruah and P. Tiwari, "Investigation of co-pyrolysis mechanism of oil shale and rubber seed shell, product yield and optimization of pyrolysis parameter using Response Surface Methodology", *Fuel*, 317, 2022.

6. Co-pyrolysis of oil shale with lignocellulosic biomass

To understand the synergy mechanism of the co-pyrolysis process, it is critical to investigate the interaction of different pyrolysis process parameters. During co-pyrolysis process, the cynical process parameters which affect the yield and composition of the pyrolysis products are pyrolysis temperature, heating rate, and feed blending ratio [241, 242]. To study the influence of these process parameters on the yield of pyrolytic oil and gases, different optimization techniques have been reported in literature [241, 243]. Among these, response surface methodology (RSM) has been established as a reliable and simplified technique to maximize or minimize the yield of different pyrolytic products [22, 159, 160].

This chapter aims to present a comprehensive study of the catalytic effect of oil shale on the composition of pyrolytic products during co-pyrolysis of Indian oil shale and rubber seed shell. In India, rubber seeds (*Hevea brasiliensis*) are found abundantly in Assam and Kerala [244]. The rubber seed kernel is used as a viable feedstock for production of biodiesel. However, the shell is generally discarded as waste [93, 245, 246]. Few studies have been reported on the use of rubber seed shell for production of bio-oil by pyrolysis [247]. Nevertheless, the pyrolytic oil produced from rubber seed shell possesses a high percentage of oxygenated compounds, thus decreasing the heating value of the bio-oil produced from rubber seed shell [245]. Therefore, the rubber seed shells acquired as laboratory waste have been subjected to co-pyrolysis with Indian oil shale to investigate the catalytic effect of oil shale on product yield and composition. The pyrolysis experiments were designed using Design–Expert software for Response Surface Methodology (RSM) optimization of pyrolysis parameters. The degradation kinetic behavior was investigated using isoconversional methods and the obtained kinetic parameters were validated by reconstruction of thermogravimetric profiles. The detailed characterization of pyrolytic products was carried out by different standard analytical techniques.

6.1. Thermogravimetric analysis of co-pyrolysis of oil shale and rubber seed shell

The degradation kinetics of co-pyrolysis of Indian oil shale (OS) and rubber seed shell (RSS) were established by using three isoconversional methods to the thermogravimetric data obtained for three blending ratios of 1:2, 1:1 and 2:1 at four heating rates of 5, 10, 20, and 30°C/min from 30°C to 1000°C. The TG-DTG curves of individual OS and RSS samples at 10°C/min is shown in Fig 6.1(a), and the co-pyrolysis curves are shown in Fig 6.1(b-d). The TG-DTG curves showed the occurrence of four distinct degradation regions corresponding to (i) moisture loss, and (ii) decomposition of hemicellulose and kerogen, (iii) cellulose, kerogen, and lignin, and (iv) mineral matter decomposition zone (Fig 6.1(a-d)). The proximate and ultimate analyses of OS and RSS have been determined on initial sample weight basis and are tabulated in Table 6.1. The OS sample showed a total degradation of 24 wt%, whereas RSS sample showed a total mass loss of 98 wt%. The degradation of OS sample showed the occurrence of three degradation zones with 4wt% moisture content from 52°C to 170°C and total organic matter (kerogen) decomposition of 20 wt%, from 300°C to 600°C. The oil shale sample contained 76 wt% of mineral matter which comprised of 46.3 % quartz, 46 % clay minerals, 5.2 % pyrite, and 2.40 % carbonates[104, 151]. The degradation of RSS appeared in four distinct zones, corresponding to moisture loss from 50°C to 170°C, decomposition of hemicellulose from 175°C to 350°C, cellulose and lignin decomposition from 350°C to 420°C, and 420°C to 550°C, respectively. The obtained degradation temperature for hemicellulose, cellulose and lignin are found to be in order the values reported in literature [93, 245]. For each blending ratio, the moisture loss curve occurred from 35°C to 200°C, and the organic matter decomposition zone ranged from 220°C to 550°C. For the temperature range of 550°C to 750°C, a third peak was observed in the DTG curve corresponding to degradation of lignin (in RSS) and mineral matter (in OS). For blending ratio of 2:1 and 1:1 (OS:RSS) the organic matter degradation curve showed the occurrence of two distinct peaks from 250°C to 500°C

corresponding to degradation of hemicellulose, cellulose, [248] and kerogen [104, 151], and from 500°C to 750°C corresponding to the simultaneous degradation of kerogen [104, 151], lignin [248], and mineral matter[151]. At blending ratio of 1:2 the organic decomposition zone, showed three distinct peaks around 350°C, 400°C and 550°C, respectively. The first peak (220°C to 400°C) and second peak (325°C to 450°C) are for decomposition of hemicellulose and cellulose, respectively[248]. The third peak (from 350°C to 650°C) occurred due to organic matter degradation (of OS) along with the initiation of lignin degradation (of RSS). The TG-DTG curves showed a total degradation of 52wt% for the mixture feed.

Table 6.1. Physicochemical properties of oil shale (OS) and rubber seed shell (RSS).

Properties	Upper Assam oil shale [151]	Rubber seed shell [245]
C (wt%)	30.06	51
H (wt%)	2.8	6.24
N (wt%)	1.44	4.1
S (wt%)	3.61	0
O ^a (wt%)	57.99	38.66
Moisture (wt%)	4.43	10.5
Ash (wt%)	53.93	0.32
Volatile matter (wt%)	31.78	75.65
Fixed carbon (wt%)	9.86	23.4

^aOxygen content have been calculated by difference [$O=100-(C+H+N+S)$]

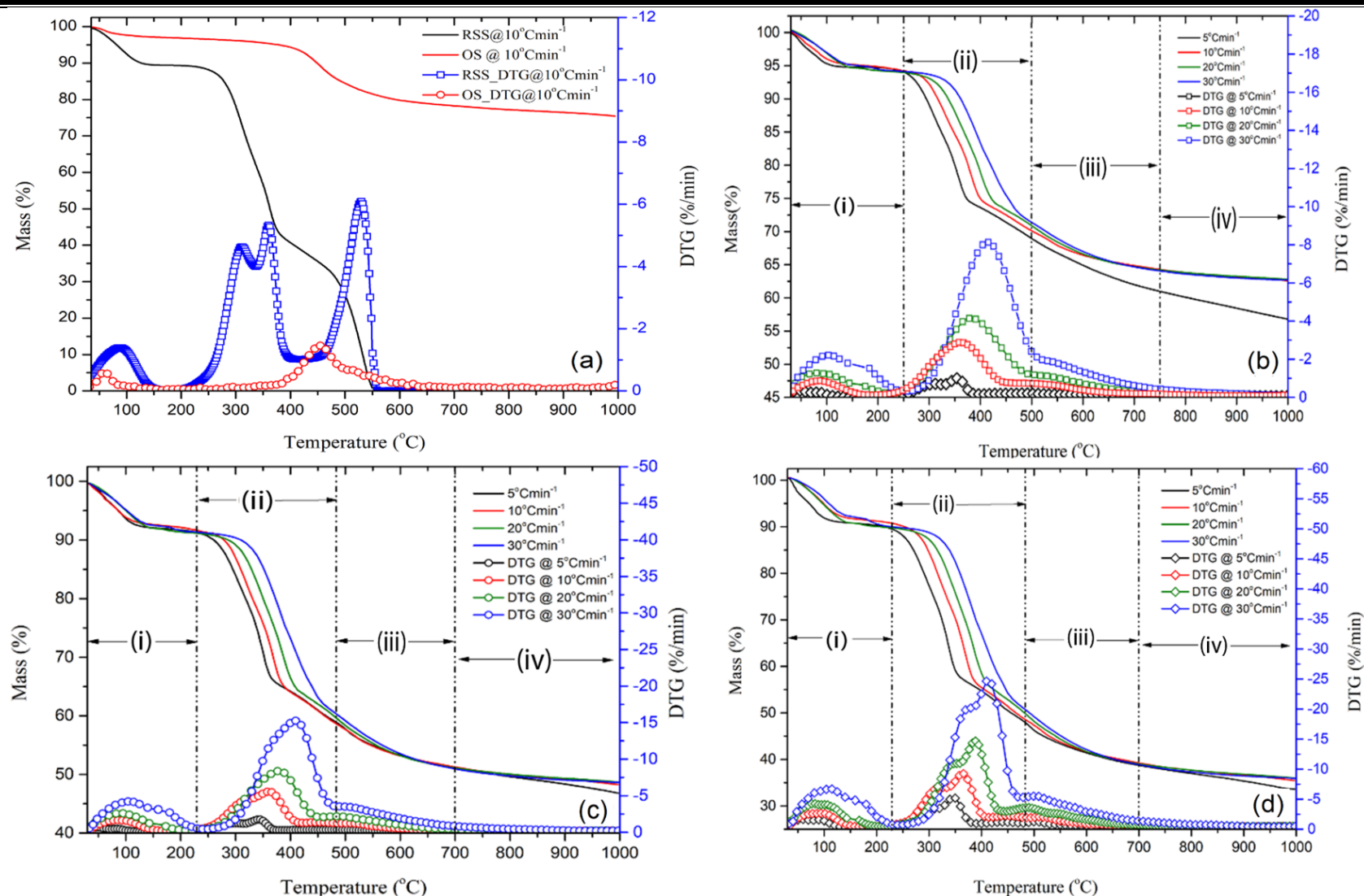


Fig 6.1. TGA-DTG curve for (a) OS and RSS heating rate of 10°C/min, and OS:RSS blending ratio of (b) 1:2, (c) 1:1, (d) 2:1, showing (i) moisture loss, (ii) hemicellulose and kerogen decomposition, (iii) cellulose, lignin, and kerogen decomposition, and (iv) mineral matter decomposition zone.

6.2. Kinetic study

6.2.1. Determination of apparent activation energy values

The organic matter decomposition zone was identified to appear from 220°C to 550°C from TG-DTG analysis and was used to determine the kinetic parameters for co-pyrolysis of OS and RSS. The step-by-step process for the determination of the kinetic triplets by Isoconversional methods is presented in section 2.13 of Chapter 2. The distribution of apparent activation values obtained using Friedman, Starink, and AIC methods are shown in Fig 6.2(a-c) for each blending ratio of 1:2, 1:1, and 2:1, respectively. AIC method showed the lowest average error value of 2.3% compared to 3.5% and 4.5% for Starink and Friedman method, respectively. For blending ratio of 1:2 (OS:RSS), AIC method showed the lowest mean activation energy of 249.5 kJmol⁻¹ compared to Friedman (257.2 kJmol⁻¹) and Starink (256.8 kJmol⁻¹). Friedman, Starink, and AIC method showed increase in apparent activation energy values from $\alpha = 0.05$ to $\alpha = 0.15$, constant from $\alpha = 0.15$ to $\alpha = 0.35$, considering error percentage and then decrease from $\alpha = 0.35$ to 0.52. The E_a values for Starink method remained constant from $\alpha = 0.52$ to 0.7 and decreased from $\alpha = 0.7$ to 0.95. However, Friedman and AIC method showed constant E_a from $\alpha = 0.52$ to 0.8, and decrease from $\alpha = 0.8$ to 0.95. For blend ratio of 1:1, Friedman and Starink method showed mean activation energy values of 299.4 kJmol⁻¹ and 289.5 kJmol⁻¹ respectively, and AIC method showed the lowest activation energy value of 270 kJmol⁻¹. For Friedman method, the apparent activation energy values remained constant from $\alpha = 0.05$ to 0.65 considering error percentage, increased from $\alpha = 0.65$ to 0.8, decreased from $\alpha = 0.8$ to 0.85 and remained constant from $\alpha = 0.85$ to 0.95. Starink method showed increase in apparent activation energy values from $\alpha = 0.05$ to 0.65 considering error percentage and decreased from $\alpha = 0.65$ to 0.95. AIC method showed constant apparent activation energy values from $\alpha = 0.05$ to 0.7 considering error percentage, and decreased from $\alpha = 0.7$ to 0.95. For blend ratio of 2:1, mean apparent activation energy values appeared to be 308 kJmol⁻¹, 305 kJmol⁻¹, and 275

kJmol^{-1} for Friedman, Starink, and AIC methods, respectively. Friedman, Starink, and AIC method showed similar trends in the apparent activation energy values distribution, increasing from $\alpha = 0.05$ to 0.8 and decreasing from $\alpha = 0.8$ to 0.95. It was observed that the apparent activation energy values increased with an increase of oil shale in the blend. Previous studies showed oil shale (OS) and rubber seed shell (RSS) exhibit the mean apparent activation energy values of $249.71 \text{ kJmol}^{-1}$ [151] and 135 kJmol^{-1} [93], respectively. The obtained average apparent activation energy values appear to be in range with the reported average apparent activation energy values for co-pyrolysis of Fushun oil shale with spirulina biomass [103].

6.2.2. Determination of reaction order and pre-exponential factor

The apparent activation energy values were used to determine the kinetic models and the values of pre-exponential factors. The kinetic models for co-pyrolysis were determined using Criado master plot [151]. The AIC method showed highest correlation ($R^2 = 0.98$) for experimental $f(\alpha)$ vs theoretical $f(\alpha)$ (Fig 6.3). The degradation kinetics of co-pyrolysis of OS and RSS showed occurrence of multiple reaction models throughout the entire degradation for each blending ratio of 1:1, 1:2, and 2:1. For blending ratio of 1:2, initially ($\alpha = 0.02$ to 0.6), F2 second order reaction model occurred and with progress it shifted to A3 Avrami Erofev nucleation model ($\alpha = 0.6$ to 0.98). The similar trends of reaction models, F2 second order reaction model ($\alpha = 0.02$ to 0.5) followed by A3 Avrami Erofev nucleation model ($\alpha = 0.52$ to 0.98) was found for blending ratio of 1:1. Further increase in the blending ratio (2:1), the degradation occurred in three steps, F2 second order ($\alpha = 0.02$ to 0.45), D3 diffusion model ($\alpha = 0.45$ to 0.6) and A3 Avrami Erofev nucleation model ($\alpha = 0.62$ to 0.98). It was observed that, second order reaction model and A3 Avrami Erofev nucleation model were dominant for each blending ratio; however, with increase in percentage of oil shale at blending ratio of 2:1, D3 diffusion reaction model appeared as an intermediate step between F2 and A3 Avrami Erofev reaction model. Previous studies have shown oil shale pyrolysis to follow D3 diffusion

and A3 Avrami Eroffev nucleation model [22, 72]. F2 second order reaction model may have occurred due to simultaneous degradation of kerogen in the oil shale, with hemicellulose and cellulose present in the rubber seed shell. The occurrence of F2 second-order reaction model has been previously observed to occur during the degradation of woody biomass [86]. The occurrence of the Avrami Eroffev nucleation model is dominant in petroleum source rocks as petroleum source rocks follow the sigoidal reaction model [51]. At a higher concentration of oil shale in the mixture, D3 diffusion-reaction model may have occurred due to production of smaller hydrocarbon compounds from the reactions on the surface of the organic matter and diffusion through the pores to the surface due to heat transfer gradient (D3 diffusion) [72].

The values of pre-exponential factor varied with the blending ratio and ranged from $4.51 \times 10^{20} \text{ sec}^{-1}$ to $3.7 \times 10^{21} \text{ sec}^{-1}$ (for 2:1 1.5×10^{21} to $2.4 \times 10^{21} \text{ sec}^{-1}$ (for 1:1), and 2.1×10^{19} to $3.02 \times 10^{20} \text{ sec}^{-1}$ (for 1:2).

6.2.3. Reconstruction of conversion profiles

The kinetic triplets obtained by each isoconversional method were used for the reconstruction of conversion (α) vs. temperature (T) profiles. The simulated vs. experimental data plots for blending ratio of 1:1 and heating rate of 5, 10, 20, and 30°C/min are presented in Fig. 6.4 (a-d) for each isoconversional method. Comparison of regression analysis (R^2) value for the isoconversional methods (Fig 6.5 (a-c)) showed AIC method to exhibit the highest average R^2 value of 0.99, followed by 0.98 and 0.96 by Starink and Friedman method respectively for each blending ratio of 1:1, 1:2, and 2:1.

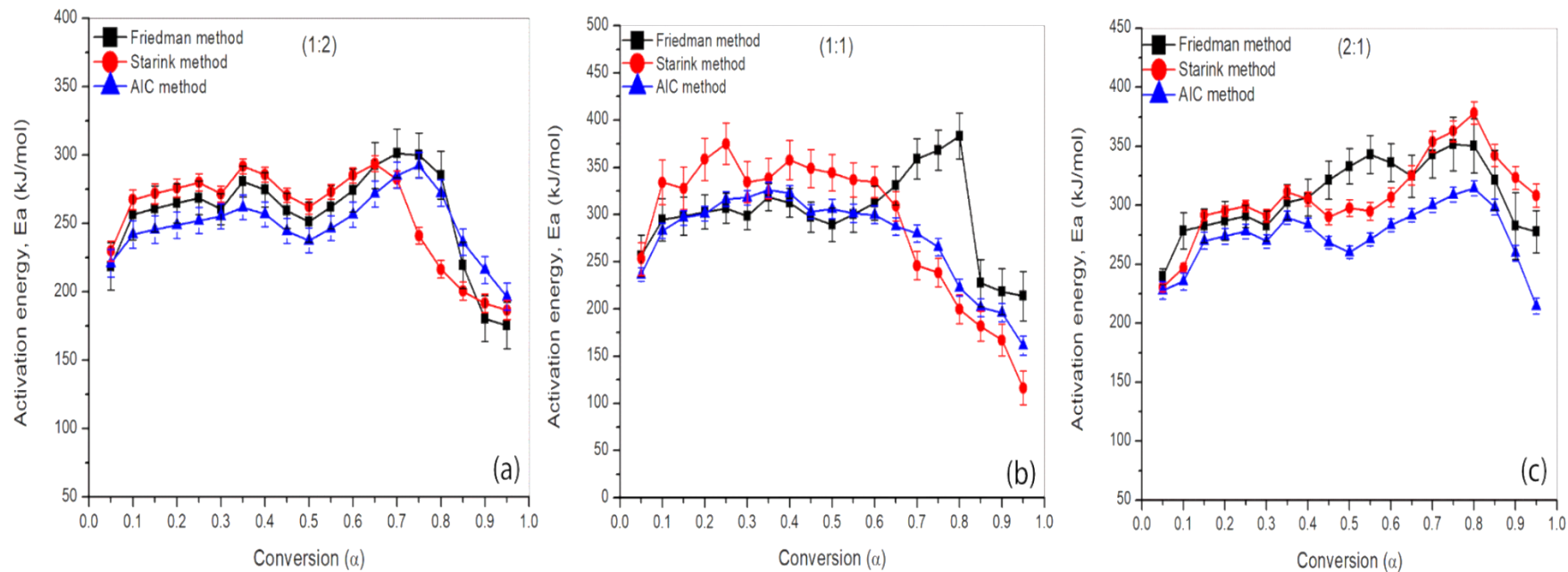


Fig 6.2. Distribution of apparent activation energy values of co-pyrolysis for OS:RSS blending ratio of (a) 1:2, (b) 1:1 and (c) 2:1 using different isoconversional methods.

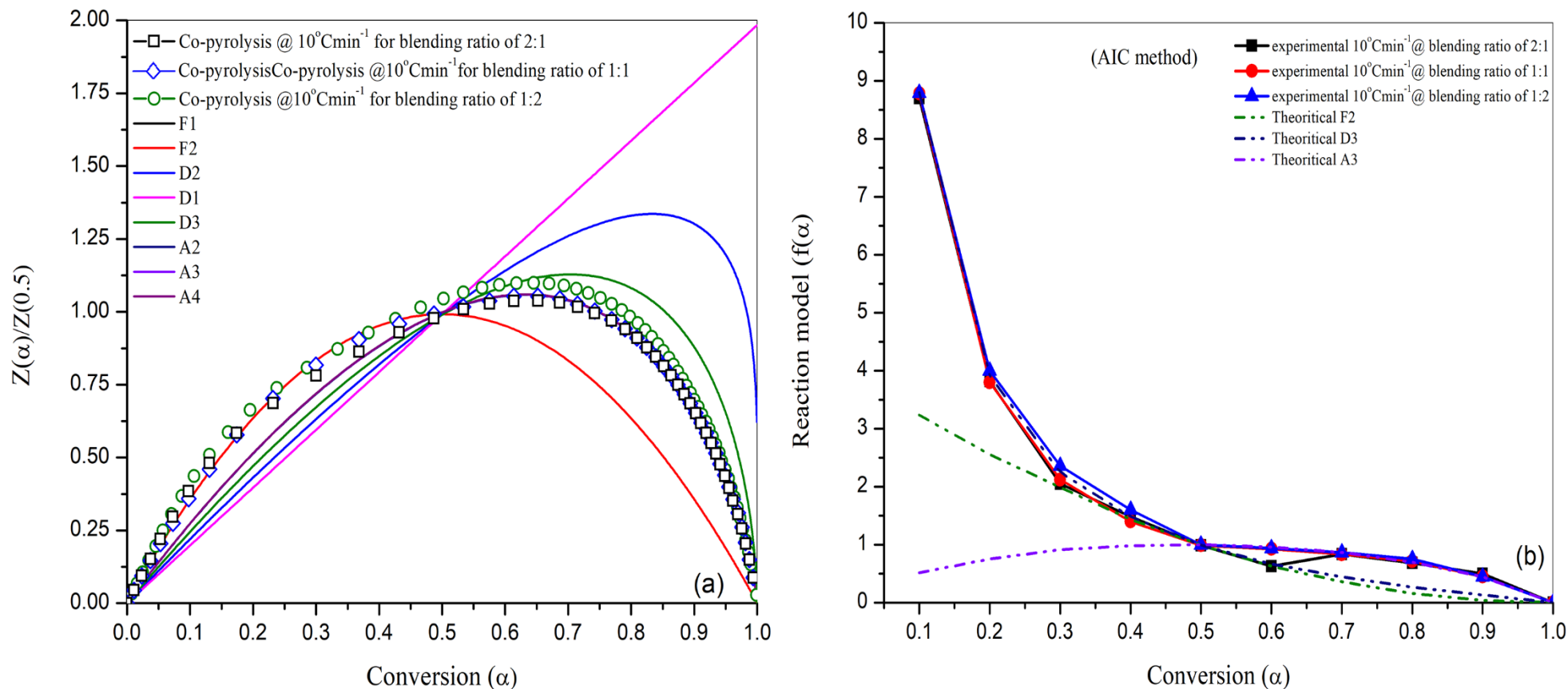


Fig 6.3. (a) Theoretical master plots of different reaction models and experimentally determined reaction models at $10^\circ\text{C}/\text{min}$ for OS:RSS blending ratio of 2:1, 1:1 and 1:2 and (b) experimental vs theoretical $f(\alpha)$ obtained for AIC method for each blending ratio.

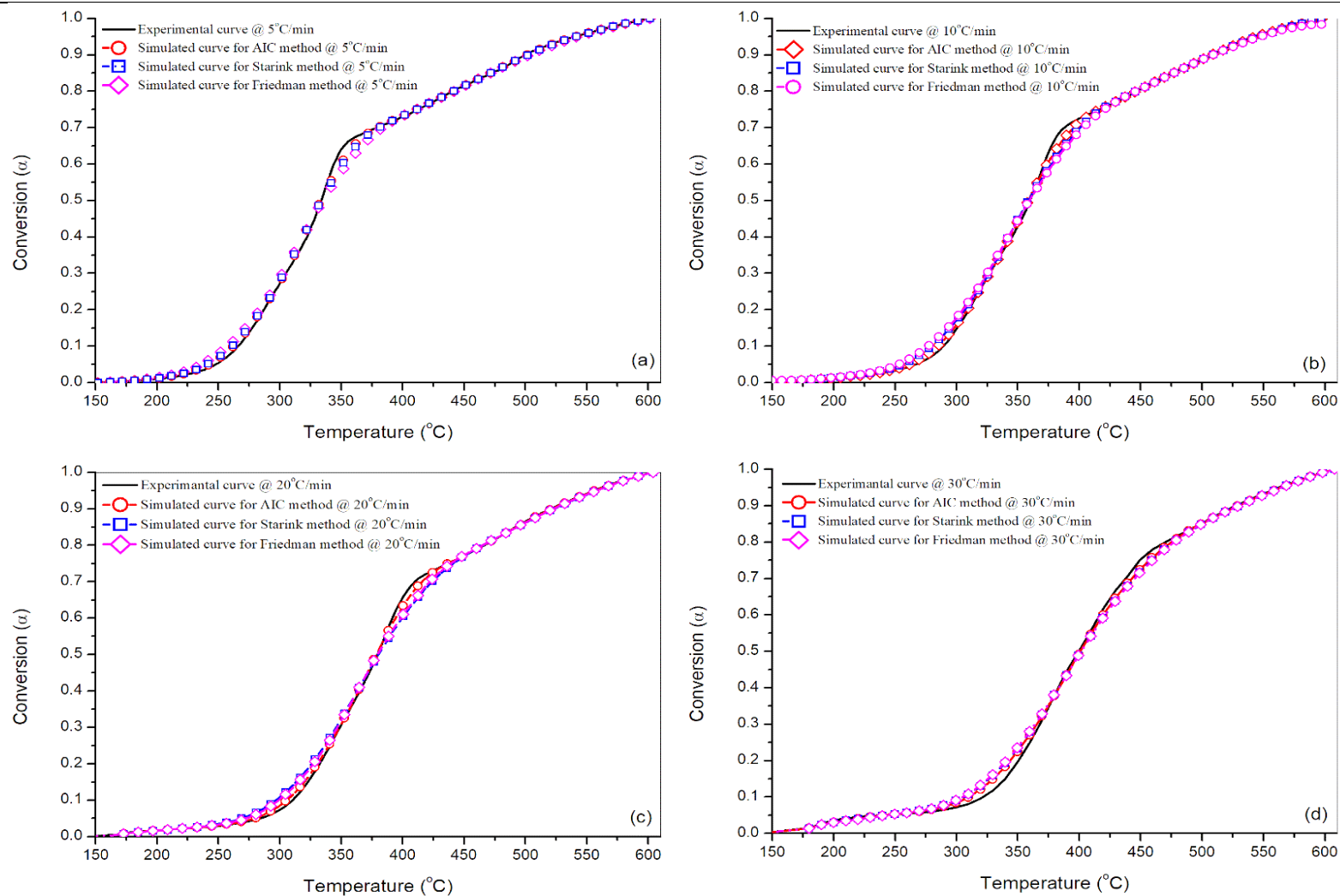


Fig 6.4. Fitness of simulation vs experimental TG profiles for AIC, Starink, Friedman method at blending ratio of 1:1 and heating rates of (a) 5 $^{\circ}\text{C}/\text{min}$, (b) 10 $^{\circ}\text{C}/\text{min}$, (c) 20 $^{\circ}\text{C}/\text{min}$, and (d) 30 $^{\circ}\text{C}/\text{min}$.

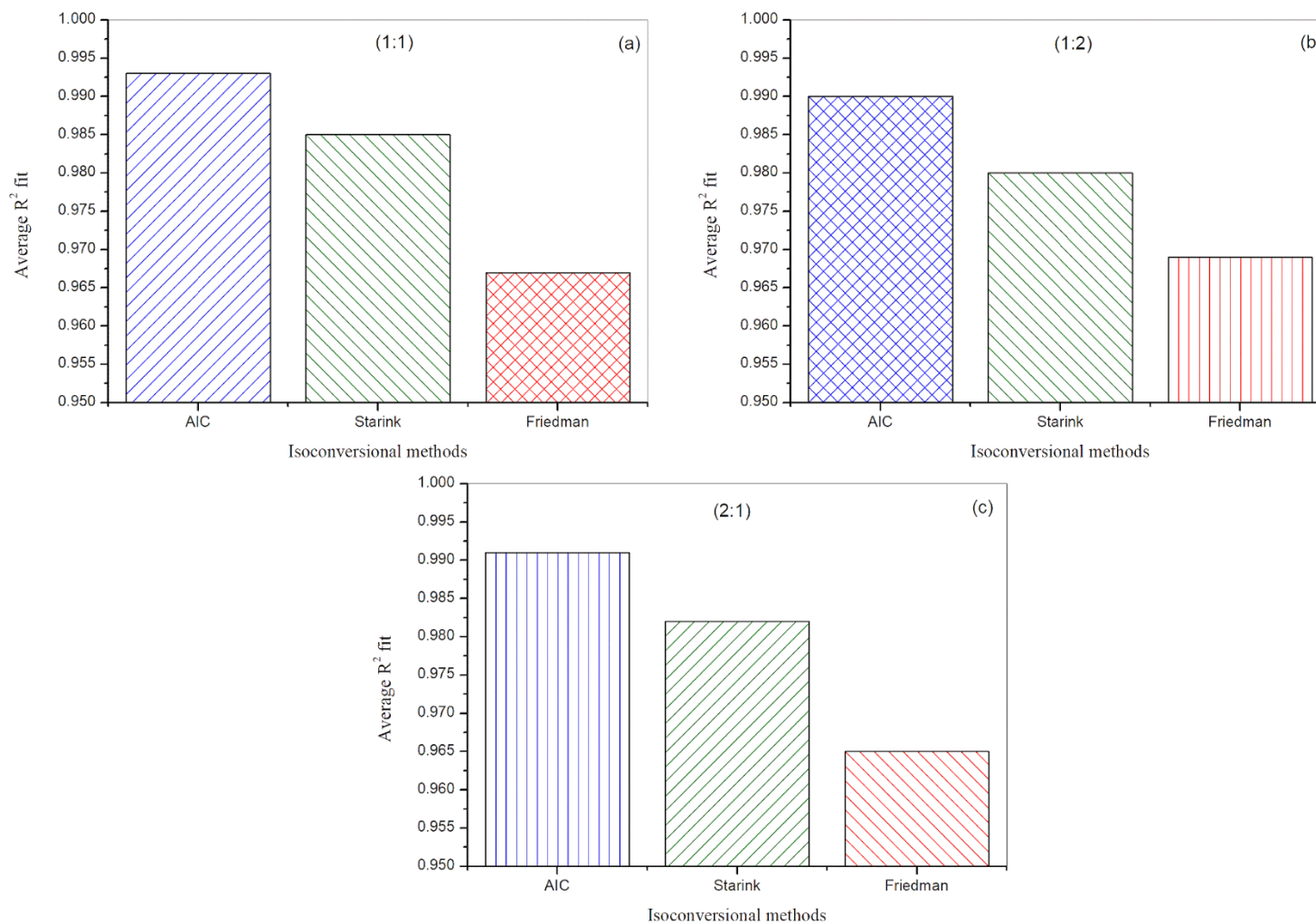


Fig 6.5. Linear fitting of different isoconversional methods for OS to RSS blending ratio of (a) 1:1, (b) 1:2, and (c) 2:1.

6.3. Lab-scale co-pyrolysis experiments

The methodology of the lab-scale co-pyrolysis experiment has been discussed in section 2.12.4 of Chapter 2. From the lab-scale co-pyrolysis experiments, it was observed that a maximum oil yield of 27 wt/wt% was obtained at a heating rate of 5°C/min and pyrolysis temperature of 550°C for blending ratio of 1:1. For blending ratio of 1:2, maximum oil yield of 24.21 wt/wt% was obtained at 550°C and 5°C/min. The experiment for blending ratio of 2:1 at 5°C/min and 600°C resulted the maximum oil yield of 20.5 wt/wt%. An increase in the percentage of oil shale in the blend leads to a decrease in oil yield with an increase in gas and char yield. The percentage of oil yield and total mass loss was directly affected by the heating rate for each blending ratio, as with an increase in the heating rate, the oil yield and total mass loss decreased. The aqueous phase yield was influenced by the percentage of RSS present in the blend and heating rate. Higher percentage of RSS led to an increase in percentage of aqueous phase due to high moisture content in RSS compared to oil shale. A low heating rate of 5°C/min significantly decreased the percentage of aqueous yield for all blending ratios. Although, pyrolysis temperature did not show any significant influence over the yield of the aqueous phase. Pyrolysis temperature showed notable influence over the total mass loss for each blend ratio. It was observed that for blending ratio of 1:2 and 1:1, the oil yield increased with increase in pyrolysis temperature from 450°C to 550°C but decreased at 600°C. Thermogravimetric analysis of RSS sample showed the degradation to occur up to 550°C. Previous studies on pyrolysis of RSS have reported that, maximum oil yield was achieved from 500°C to 550°C [93, 245]. It can be observed that the degradation of the sample at blend ratio of 1:2 and 1:1 showed similar properties to that of RSS. Therefore, it may be assumed that at OS:RSS blending ratio of 1:2 and 1:1 the RSS appeared to be the dominant feed. The decrease in oil yield at 600°C may have occurred due to the occurrence of the secondary reactions leading to cracking and coking of the produced hydrocarbon vapors. Conversely, for a blend ratio of 2:1

the maximum oil yield was observed at 600°C. In our previous studies [22], it was observed that during pyrolysis of Indian oil shale, the maximum oil yield was achieved at 600°C at a heating rate of 10°C/min. As, at blend ratio of 2:1 the percentage of oil shale is double than the percentage of RSS, the oil shale may have acted as the dominant feed in the mixture. Previous studies have also reported that the presence of oil shale delays the thermal degradation of the organic matter in biomass samples [103]. The gas yield for the entire set of experimental matrix showed a reverse trend to oil yield as with increase in oil yield the gas yield decreased and vice versa (Table 6.2).

The significance and reliability of the data obtained from the optimization model was evaluated from the p-value of the analysis of variance (ANOVA) equations for each response (Eq.6.1-6.5).

$$\text{Mass loss} = 46.56 + 5.06A - 0.35B + 3.35C - 0.33AB + 1.30AC - 0.08BC - 1.3A^2 + 0.078B^2 - 1.53C^2 - 0.01ABC + 0.69A^2B + 5.98A^2C - 4.10B^2C - 0.63C^3 \quad (6.1)$$

$$\text{Oil yield} = 23.05 + 2.60A - 1.01B + 2.26C + 0.33AB + 0.09AC - 0.28BC - 1.02A^2 + 1.06B^2 - 1.14C^2 + 0.28ABC + 0.80A^2B - 3.06A^2C - 1.93AB^2 + 3.5B^2C - 0.83C^3 \quad (6.2)$$

$$\text{Gas Yield} = 13.75 + 0.57A + 2.20B + 0.72C - 0.85AB + 0.12AC - 0.45BC + 1.28A^2 - 1.56B^2 + 0.009C^2 - 0.81ABC - 1.82A^2B + 0.4A^2C + 0.76AB^2 + 1.24B^2C + 0.57C^3 \quad (6.3)$$

$$\text{Aqueous phase} = 9.55 + 1.8A - 0.43B - 0.84C - 0.18AB + 0.47AC + 0.27BC - 1.44A^2 - 0.009B^2 - 0.36C^2 + 0.14ABC + 0.23A^2B + 1.98A^2C - 0.85AB^2 - 1.44B^2C + 0.41C^3 \quad (6.4)$$

$$\text{Char yield} = 53.43 - 5.06A + 0.35B - 4.35C + 0.33AB - 1.31AC + 0.08BC + 1.31A^2 - 0.08B^2 + 1.53C^2 + 0.01ABC - 0.69A^2B - 5.98A^2C + 1.48AB^2 + 4.11B^2C + 0.64C^3 \quad (6.5)$$

Where, A=Blending ratio; B= Heating rate (°C/min); C = Temperature (°C).

The significance of the considered parameters (ANOVA) for oil, mass loss, gas yield, aqueous phase, and char yield are tabulated in Table 6.3-6.8. The plots for the model predicted values vs. the actual or experimental values for each response are presented in Fig 6.6. The CCD model suggested F value of 49.41 and p-value less than 0.0001 for mass loss, F value of 24.58 and p-value of 0.0035 for oil yield, F-value of 16.47 and p-value of 0.0075 for gas yield, F value of 8.51 and p-value of 0.0258 for aqueous phase and F value of 50.59 and p-value less than 0.0001. The obtained F-values are in the range of the predicted and experimental (actual) values for each parameter, and the p-values are lesser than 0.05 for each response. This shows that the obtained experimental values are significant and therefore acceptable [162, 249, 250]. For mass loss, oil yield, and char yield, the blending ratio, and pyrolysis temperature showed p-values less than 0.05 and appeared as significant parameters. For gas yield, the heating rate showed p-value less than 0.05, therefore, being the significant parameter. For the aqueous phase, the blending ratio appeared to be the influential parameter with p-value less than 0.05. It was observed that the blending ratio appeared to be the significant parameter for all responses except for gas yield. For mass loss, the statistically determined R^2 value for the fitted model appeared to be 0.97, which indicated that 97% of the experimentally obtained results showed consistency with the predicted data for the selected model. Similarly, oil yield, gas yield, aqueous phase, and char yield exhibited R^2 values of 0.98, 0.98, 0.96, and 0.97, respectively. The least consistency was observed for the aqueous phase with a consistency of 0.96 or 96%. A similar result was observed for the optimization of pyrolysis parameters of Indian oil shale [22]. The surface plots of the optimum condition are highlighted and shown in Fig 6.7 (a-e). It was observed that, for mass loss, oil yield and aqueous phase the stationary points appeared as saddle points (Fig 6.7 (a, b and d)). The occurrence of the surface plots in saddle nature signifies that the interaction between the corresponding variables is significant [251]. It may be noted that from the ANOVA analysis the parameter “blending ratio” appeared to be influential for

mass loss, oil yield and aqueous phase. The percentage of mass loss and oil yield increased with increase in RSS in the blending ratio. Again, biomass pyrolysis produces high concentration of aqueous soluble organic compounds [252, 253]. Therefore, the aqueous phase content increased with increase in concentration of RSS in the blend. The most desired values for the co-pyrolysis process were obtained under the condition of blending ratio of 1:1, at a heating rate of 5°C/min and pyrolysis temperature of 550°C. The model predicted maximum mass loss of 44.96 wt/wt% oil yield of 28.5 wt/wt%, gas yield of 10.90 wt/wt%, aqueous phase of 8.25 wt/wt%, and char yield of 52.35 wt/wt%. The oil samples obtained at the optimum pyrolysis condition showed gross calorific value (GCV) of 32 MJ/kg, with flash point and flame point of 47°C and 58°C, respectively. The pour point of the oil sample was observed to be 4°C, and carbon residue was calculated as 0.33 wt/wt%.

Table 6.2. Experimental design matrix with model suggested parameters and corresponding experimental responses.

Run	Factors			Response									
	Blending ratio(OS:RSS)	Heating rate (°C/min)	Temperature (°C)	Mass loss (wt%)		Oil yield (wt/wt%)		Gas yield (wt/wt%)		Aqueous phase (wt/wt%)		Char yield (wt/wt%)	
				actual	predicted	actual	predicted	actual	predicted	actual	predicted	actual	predicted
1	1.25	12.5	525	45.99	45.01	23.66	23.25	13.48	12.50	7.85	9.26	55.01	54.99
2	1	10	550	47.82	46.54	23.76	24.01	14.39	14.50	9.67	8.03	52.18	53.46
3	0.5	5	550	43.9	44.21	24.21	24.25	13.37	13.75	5.12	6.21	57.40	55.79
4	2	5	600	40.37	41.30	20.5	20.61	10.97	11.20	8.9	9.49	59.63	58.70
5	0.5	20	450	36.7	35.91	19.5	20.10	10.19	10.20	7.01	5.61	63.3	64.09
6	2	20	600	54.2	54.71	24.75	25.01	18.15	18.55	9.3	11.15	47.8	45.29
7	2	20	450	40.6	41.01	20.75	21.05	12.55	12.55	7.3	7.41	59.4	58.99
8	1.25	12.5	600	48.91	45.31	23.03	22.85	14.99	15	9.89	7.46	52.09	54.69
9	2	5	600	54.35	52.71	24.5	23.75	19.6	20	9.25	8.96	46.65	47.29
10	0.5	10.5	525	40.2	40.65	19.43	19.43	14.46	14.50	6.31	6.72	59.8	59.35
11	1	5	550	46.91	47.20	27	28.5	11.31	10.90	7.1	8.25	54.09	52.35
12	1	25	525	46.2	45.75	24.31	24.51	13.08	11.10	8.81	10.14	53.8	54.25
13	1.25	12.5	525	46.34	45.01	23.31	23.66	13.52	14.05	9.51	7.3	53.66	54.99
14	1.25	10	550	48.02	49.32	23.57	24.01	14.62	15.05	8.83	10.26	52.98	50.68
15	0.5	20	600	45.11	44.95	22	22	16.56	17.10	6.55	5.9	54.89	55.05
16	1.25	12.5	650	46.54	46.32	19.88	20.01	17.63	18.10	9.03	15.34	53.46	53.68
17	1.25	12.5	400	37.98	37.04	20.05	20.55	9.88	10.88	8.05	6.14	62.02	62.96
18	1.25	10	500	45.5	47.20	21.55	21.75	14.22	14.50	9.73	10.95	54.5	52.80
19	0.5	5	450	35.2	36.71	19.43	20.01	8.46	9.20	7.31	7.50	64.8	63.29
20	2.5	12.5	525	51.37	51.70	24.55	25.55	18.27	19.10	8.55	7.14	48.63	48.30

Table 6.3. ANOVA table for the experimental design results of RSM for oil yield.

Source	Sum of Squares	df	Mean Square	F-value	p-value	Significance
Model	92.51	15	6.17	24.58	0.0035	significant
A-Blending ratio(rss:os)	14.18	1	14.18	56.53	0.0017	
B-Heating rate	0.6915	1	0.6915	2.76	0.1722	
C-Temperature	3.03	1	3.03	12.06	0.0255	
AB	0.8712	1	0.8712	3.47	0.1359	
AC	0.0648	1	0.0648	0.2583	0.6380	
BC	0.6498	1	0.6498	2.59	0.1828	
A ²	3.84	1	3.84	15.30	0.0174	
B ²	2.96	1	2.96	11.81	0.0264	
C ²	13.57	1	13.57	54.07	0.0018	
ABC	0.6498	1	0.6498	2.59	0.1828	
A ² B	0.4059	1	0.4059	1.62	0.2723	
A ² C	0.2288	1	0.2288	0.9119	0.3937	
AB ²	6.19	1	6.19	24.69	0.0077	
AC ²	0.0000	0				
B ² C	0.3038	1	0.3038	1.21	0.3329	
BC ²	0.0000	0				
A ³	0.0000	0				
B ³	0.0000	0				
C ³	2.73	1	2.73	10.90	0.0299	
Residual	1.00	4	0.2509			
Lack of Fit	0.9085	2	0.4542	9.56	0.0947	not significant
Pure Error	0.0951	2	0.0475			
Standard Deviation	0.5009	R ²	0.9893			
Mean	22.48	Adjusted R ²	0.9490			
Coefficient of variance (%)	2.23	Predicted R ²	0.9820			

Table 6.4. ANOVA table for the experimental design results of RSM for mass loss.

Source	Sum of Squares	df	Mean Square	F-value	p-value	Significance
Model	533.77	15	35.58	44.41	< 0.0001	significant
A-Blending ratio(rss:os)	53.65	1	53.65	1.61	< 0.0001	
B-Heating rate	0.0826	1	0.0826	0.4492	0.5394	
C-Temperature	11.20	1	11.20	60.88	0.0015	
AB	0.8646	1	0.8646	4.70	0.0961	
AC	13.70	1	13.70	74.47	0.0010	
BC	0.0561	1	0.0561	0.3050	0.6102	
A ²	6.28	1	6.28	34.11	0.0043	
B ²	0.0161	1	0.0161	0.0876	0.7820	
C ²	24.71	1	24.71	134.32	0.0003	
ABC	0.0010	1	0.0010	0.0055	0.9444	
A ² B	0.3035	1	0.3035	1.65	0.2684	
A ² C	0.8759	1	0.8759	4.76	0.0945	
AB ²	3.66	1	3.66	19.87	0.0112	
AC ²	0.0000	0				
B ² C	0.4073	1	0.4073	2.21	0.2110	
BC ²	0.0000	0				
A ³	0.0000	0				
B ³	0.0000	0				
C ³	1.58	1	1.58	8.58	0.0428	
Residual	0.7360	4	0.1840			
Lack of Fit	0.6547	2	0.3274	8.06	0.1104	not significant
Pure Error	0.0813	2	0.0406			
Standard Deviation	0.4289	R ²	0.9986			
Mean	45.11	Adjusted R ²	0.9935			
Coefficient of variance (%)	0.9509	Predicted R ²	0.9956			

Table 6.5. ANOVA table for the experimental design results of RSM for gas yield.

Source	Sum of Squares	df	Mean Square	F-value	p-value	Significance
Model	159.66	15	10.64	16.47	0.0075	significant
A-Blending ratio(rss:os)	0.6862	1	0.6862	1.06	0.3610	
B-Heating rate	3.26	1	3.26	5.05	0.0880	
C-Temperature	0.3109	1	0.3109	0.4811	0.5261	
AB	5.76	1	5.76	8.92	0.0405	
AC	0.1128	1	0.1128	0.1746	0.6975	
BC	1.59	1	1.59	2.47	0.1915	
A ²	6.07	1	6.07	9.39	0.0375	
B ²	6.42	1	6.42	9.93	0.0345	
C ²	0.0010	1	0.0010	0.0016	0.9700	
ABC	5.27	1	5.27	8.15	0.0462	
A ² B	2.06	1	2.06	3.18	0.1490	
A ² C	0.0040	1	0.0040	0.0062	0.9411	
AB ²	0.9693	1	0.9693	1.50	0.2879	
AC ²	0.0000	0				
B ² C	0.0369	1	0.0369	0.0571	0.8229	
BC ²	0.0000	0				
A ³	0.0000	0				
B ³	0.0000	0				
C ³	1.28	1	1.28	1.99	0.2314	
Residual	2.58	4	0.6462			
Lack of Fit	2.04	2	1.02	3.73	0.2116	not significant
Pure Error	0.5468	2	0.2734			
Standard Deviation	0.8039	R ²	0.9841			
Mean	13.80	Adjusted R ²	0.9243			
Coefficient of variance (%)	5.82	Predicted R ²	0.9921			

Table 6.6. ANOVA table for the experimental design results of RSM for aqueous phase.

Source	Sum of Squares	df	Mean Square	F-value	p-value	Significance
Model	25.60	15	1.71	8.51	0.0258	significant
A-Blending ratio(rss:os)	6.80	1	6.80	33.89	0.0043	
B-Heating rate	0.1246	1	0.1246	0.6208	0.4748	
C-Temperature	0.4180	1	0.4180	2.08	0.2224	
AB	0.2738	1	0.2738	1.36	0.3076	
AC	1.80	1	1.80	9.00	0.0400	
BC	0.5940	1	0.5940	2.96	0.1604	
A ²	7.64	1	7.64	38.09	0.0035	
B ²	0.0002	1	0.0002	0.0012	0.9738	
C ²	1.36	1	1.36	6.75	0.0601	
ABC	0.1568	1	0.1568	0.7815	0.4266	
A ² B	0.0322	1	0.0322	0.1604	0.7093	
A ² C	0.0957	1	0.0957	0.4772	0.5277	
AB ²	1.22	1	1.22	6.07	0.0694	
AC ²	0.0000	0				
B ² C	0.0498	1	0.0498	0.2483	0.6444	
BC ²	0.0000	0				
A ³	0.0000	0				
B ³	0.0000	0				
C ³	0.6564	1	0.6564	3.27	0.1448	
Residual	0.8026	4	0.2007			
Lack of Fit	0.0950	2	0.0475	0.1343	0.8816	not significant
Pure Error	0.7076	2	0.3538			
Standard Deviation	0.4479	R ²	0.9696			
Mean	8.40	Adjusted R ²	0.8556			
Coefficient of variance (%)	5.33	Predicted R ²	0.9761			

Table 6.7. ANOVA table for the experimental design results of RSM for char yield.

Source	Sum of Squares	df	Mean Square	F-value	p-value	Significance
Model	533.77	15	35.58	53.5	< 0.0001	significant
A-Blending ratio(rss:os)	53.65	1	53.65	291.61	< 0.0001	
B-Heating rate	0.0826	1	0.0826	0.4492	0.5394	
C-Temperature	11.20	1	11.20	60.88	0.0015	
AB	0.8646	1	0.8646	4.70	0.0961	
AC	13.70	1	13.70	74.47	0.0010	
BC	0.0561	1	0.0561	0.3050	0.6102	
A ²	6.28	1	6.28	34.11	0.0043	
B ²	0.0161	1	0.0161	0.0876	0.7820	
C ²	24.71	1	24.71	134.32	0.0003	
ABC	0.0010	1	0.0010	0.0055	0.9444	
A ² B	0.3035	1	0.3035	1.65	0.2684	
A ² C	0.8759	1	0.8759	4.76	0.0945	
AB ²	3.66	1	3.66	19.87	0.0112	
AC ²	0.0000	0				
B ² C	0.4073	1	0.4073	2.21	0.2110	
BC ²	0.0000	0				
A ³	0.0000	0				
B ³	0.0000	0				
C ³	1.58	1	1.58	8.58	0.0428	
Residual	0.7360	4	0.1840			
Lack of Fit	0.6547	2	0.3274	8.06	0.1104	not significant
Pure Error	0.0813	2	0.0406			
Standard Deviation	0.84289	R ²	0.9986			
Mean	54.89	Adjusted R ²	0.9935			
Coefficient of variance (%)	0.7815	Predicted R ²	0.9921			

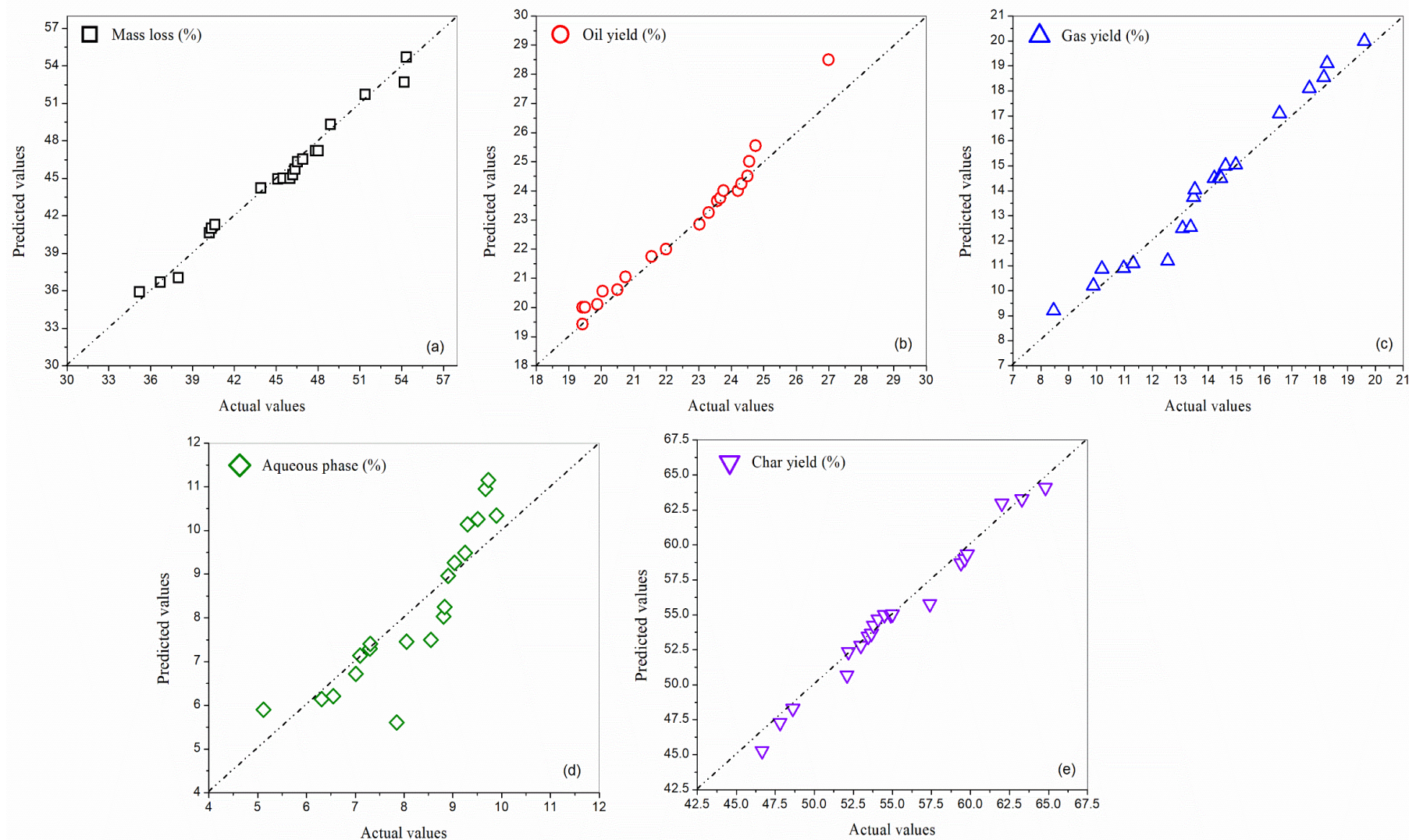


Fig 6.6. Predicted vs. actual data plot for considered responses of (a) mass loss, (b) oil yield, (c) gas yield, (d) aqueous phase and, (e) char yield.

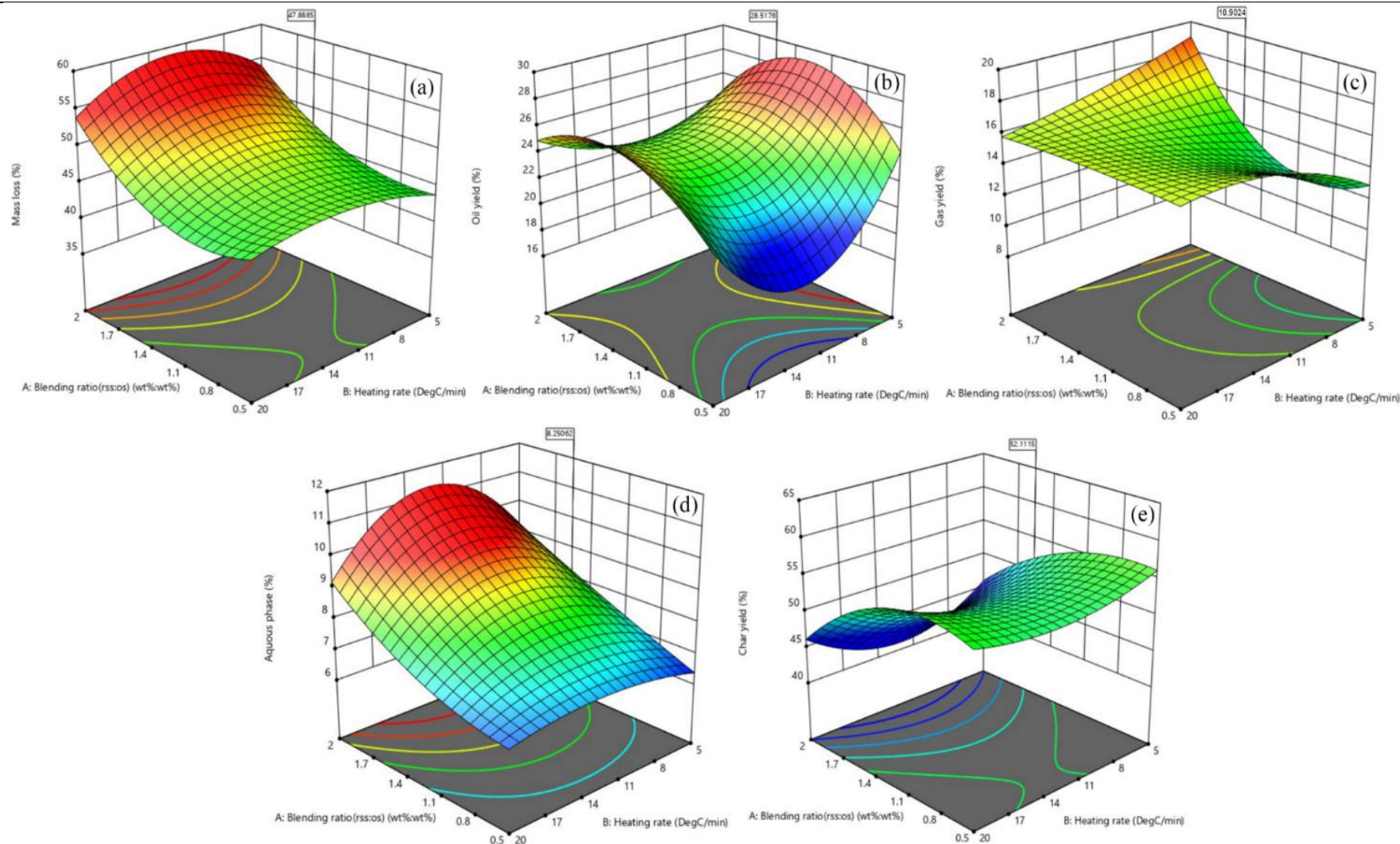


Fig 6.7. Surface plots showing the effect of process parameters with actual factor as pyrolysis temperature of 550°C in (a) mass loss, (b) oil yield, (c) gas yield, (d) aqueous phase, and (e) char yield.

6.4. Characterization of pyrolytic products

6.4.1. Fourier transform infrared spectroscopy (FTIR) analysis

FTIR (ATR) spectra of pyrolytic oil sample obtained during the optimum condition for co-pyrolysis of oil shale with rubber seed shell is shown in Fig 6.8(a). The spectra of the oil samples obtained from individual pyrolysis of oil shale and rubber seed shell sample are shown in Fig 6.8(b). The identified functional groups corresponding to their wavenumber are summarized in Table 6.8, and the concentration of identified functional groups are tabulated in Table 6.9. The oil obtained from pyrolysis of oil shale (OS) sample showed 32.4% aliphatic, 24.6% aromatics, 16.7% phenolics, ethers, and alcohols, 11.5% C=O, and 14.6% OH compounds. On the other hand, the oil obtained from pyrolysis of RSS showed 14.8% aliphatics, 17.7% aromatics, 30.6% phenolics, esters, and alcohols, 11.21% C=O compounds, and 25.7% OH group compounds. The FTIR spectra of the oil obtained at the optimum condition of 1:1 blending ratio, and 550°C at 5°C/min is compared with pyrolytic oil obtained at blending ratio of 1:2 and 2:1 at 5°C/min and pyrolysis temperature of 550°C to study the catalytic effect of oil shale on the composition of the co-pyrolytic oil. FTIR-ATR analysis showed a significant reduction in compounds containing –OH group (3300 to 3500 cm^{-1}) in the oil samples obtained from each blending ratio. It was observed that the co-pyrolytic oil obtained during the optimum condition at blending ratio of 1:1, heating rate of 5°C/min and pyrolysis temperature of 550°C showed significant reduction in methoxy (-OH) group and increase in the percentage of aliphatic compounds compared to oil obtained at blending ratio of 1:2. The oil obtained at a blending ratio of 2:1, showed a further increase in the percentage of aliphatic and aromatic compounds, with a slight decrease in oxygenated compounds at the heating rate of 5°C/min and pyrolysis temperature of 550°C. The decrease in concentration of –OH compounds was previously reported by Chen et al. [96] due to deoxygenation reaction resulting from the biomass-kerogen reaction. Similar findings were reported by Chen et al. [87], who

stated that the degradation of clay mineral matter present in oil shale has a catalytic effect on the cracking of oxygenated compounds leading to the production of higher concentrations of CO₂.

The FTIR analysis of the co-pyrolytic oil showed the catalytic behavior of oil shale (OS) over rubber seed shell (RSS). Comparison of the FTIR spectra of pyrolytic shale oil and pyrolytic oil obtained from rubber seed shell (Fig 6.8 (b)) showed a broad intensity of –OH group in rubber seed shell pyrolytic oil but the absence of aliphatic groups. Pyrolytic shale oil showed the sharp band corresponding to aliphatic compounds, along with bands corresponding to phenols, aromatics, C=O and COOH compounds. The co-pyrolytic oil appeared as a synergistic mixture of the individual pyrolytic oils with a significant increase in the intensity of aliphatic compounds. This may have occurred due to cracking and nucleation mechanism, as observed during the kinetic study of co-pyrolysis process (section 6.2.2).

Table 6.8. Functional groups corresponding to different wavenumbers [22, 72].

Wavenumbers(cm ⁻¹)	Functional Groups
3625	-OH group; Alcohols and Phenols (strong; sharp)
3300-3500	-OH stretch from –COOH and –COH
3000-2500	C-H stretch; Alkanes
1600-1650	Aromatics (Phenolic), –C=O vibration; -
1400-1600	C=O stretch from H-bonded conjugate Aromatics
860-680	Aromatic C-H Stretch;
680-610	S-O bending; sulfates

Table 6.9. Relative concentration of identified functional groups.

Wavenumber (cm ⁻¹)	Functional Groups	OS oil (%)	RSS oil (%)	Blend 1:2 (%)	Blend 1:1 (%)	Blend 2:1 (%)
3000	CH (aliphatic)	32.4	14.8	20.1	23.3	26.7
3300	-OH	14.6	25.7	21.7	17.2	15.3
1600	C=O	11.5	11.21	12.3	15.1	10
1458	Aromatics	12.6	2.5	5.7	6.2	7.2
1000-1200	Phenolic, ether and alcohol	16.7	30.6	22	19	20.8
600-800	Aromatics	12	15.2	17.2	19.2	20

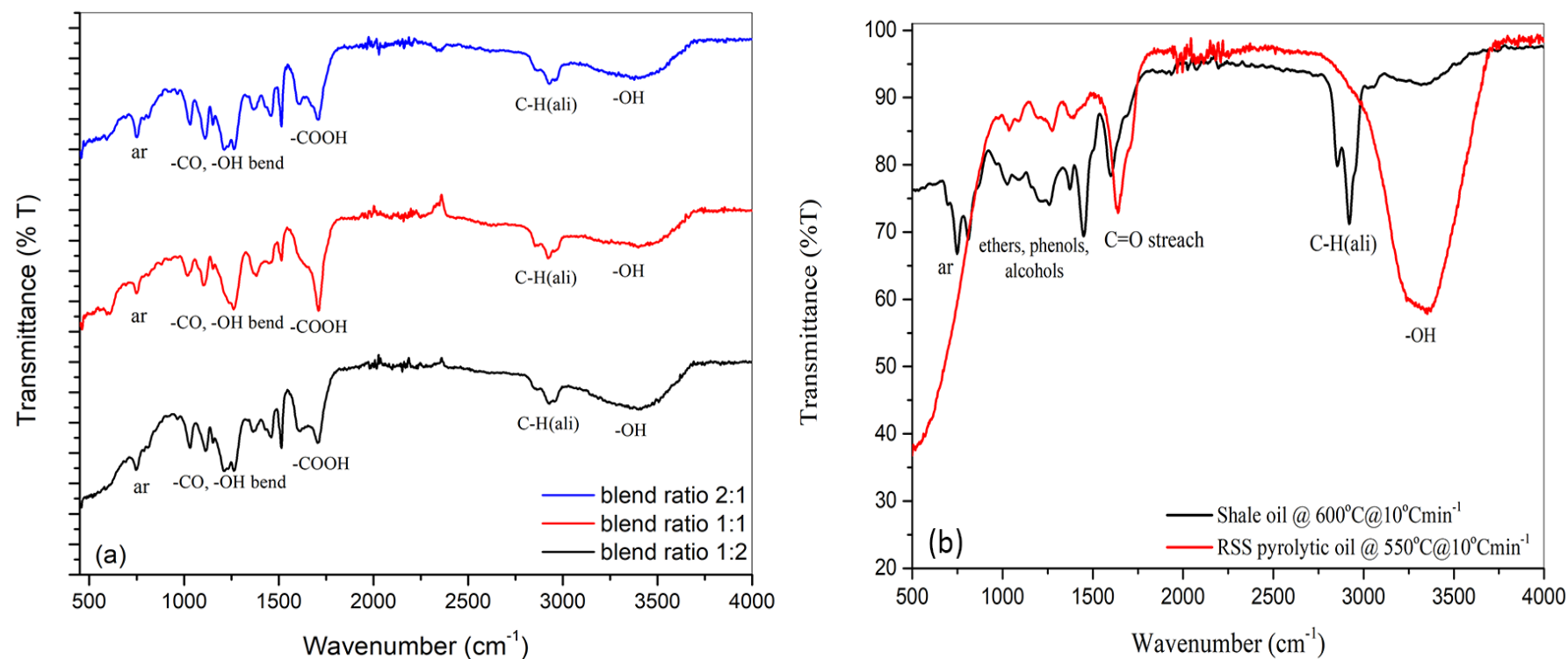


Fig 6.8. FTIR (ATR) spectra of (a) pyrolytic oil derived from co-pyrolysis experiments at $5^\circ\text{C}/\text{min}$ and 550°C for blending ratio of 2:1, 1:1, and 1:2 and (b) pyrolytic oils obtained separately from oil shale and rubber seed shell.

6.4.2. Gas chromatography (GC) analysis of pyrolytic gas

The pyrolytic gases obtained during the co-pyrolysis experiments showed the presence of permanent gases such as hydrogen (H_2), carbon monoxide (CO) and carbon dioxide (CO_2), and hydrocarbon gases from carbon number C_1 to C_5 . The relative concentration of the identified permanent and hydrocarbon gases is presented in Table 6.10 and Fig 6.9. At pyrolysis condition of $5^\circ C/min$, $550^\circ C$, and blending ratio of 1:2, the relative concentration of methane (CH_4) increased from $350^\circ C$ to $500^\circ C$ and decreased from $500^\circ C$ to $550^\circ C$. In the blending ratio of 1:1, the concentration of methane was highest at $300^\circ C$ and gradually decreased from $300^\circ C$ to $550^\circ C$. However, in the blending ratio of 2:1, the concentration of methane remained constant from $300^\circ C$ to $450^\circ C$, and decreased from $450^\circ C$ to $550^\circ C$. For the gas samples obtained from pyrolysis of OS, the concentration of CH_4 decreased with increase in pyrolysis temperature from $300^\circ C$ to $550^\circ C$. During pyrolysis of RSS, the concentration of methane decreased from $300^\circ C$ to $450^\circ C$, with a sharp increase at $500^\circ C$ and then decreased from $500^\circ C$ to $550^\circ C$. At blending ratio of 1:2, the concentration of CO decreased with increase in pyrolysis temperature from $300^\circ C$ to $550^\circ C$. However, for gases produced for blending ratio of 1:1, the concentration of CO increased with increase in pyrolysis temperature. For blending ratio of 2:1, the concentration of CO remained constant throughout the entire conversion range. For the gases during pyrolysis of RSS, the concentration of CO remained constant throughout from $300^\circ C$ to $550^\circ C$. The concentration of CO_2 increased from $300^\circ C$ to $500^\circ C$, and decreased from $500^\circ C$ to $550^\circ C$. However, during pyrolysis of OS, the concentration of CO and CO_2 increased $350^\circ C$ to $450^\circ C$, increased from $450^\circ C$ to $550^\circ C$. The concentration of CO_2 decreased with an increase in the concentration of oil shale (OS) in the blend and increase in pyrolysis temperature. Similar findings have been previously reported by Chen et al. [87], who reported that such behavior in generation of CO_2 may have occurred because oil shale tends to promote the decomposition of oxygenated compounds in the biomass leading to higher

interaction of oxygen-containing free radicals with C=O compounds in kerogen intermediates. For the gas samples collected from OS pyrolysis, the concentration of C₂ hydrocarbon gases decreased from 350°C to 550°C, and C₃, C₄, and C₅ gases increased from 350°C to 550°C. Again, during pyrolysis of RSS, the concentration of C₂ and C₃ compounds decreased from 300°C to 500°C, and increased from 500°C to 550°C, with an exception for C₃H₈, which showed decrease in concentration from 300°C to 550°C. The concentration of C₄ compounds increased from 300°C to 450°C, and decreased from 450°C to 550°C. However, the concentration of C₅ compounds increased from 300°C to 550°C. For blending ratio of 1:1 and 1:2, the concentration of C₂ and C₃ compounds increased with an increase in pyrolysis temperature from 300°C to 550°C. However, for the blending ratio of 2:1, the concentration of C₂ and C₃ compounds decreased with an increase in pyrolysis temperature from 300°C to 550°C. For the blending ratio of 1:2, the concentration of C₄ and C₅ compounds increased gradually from 300°C to 550°C. Nevertheless, for blending ratio of 1:1, the concentration of C₄ and C₅ compounds increased from 300°C to 450°C, and gradually decreased from 450°C to 550°C. For the blending ratio of 2:1, the concentration of C₄ and C₅ gases increased significantly from 300°C to 550°C.

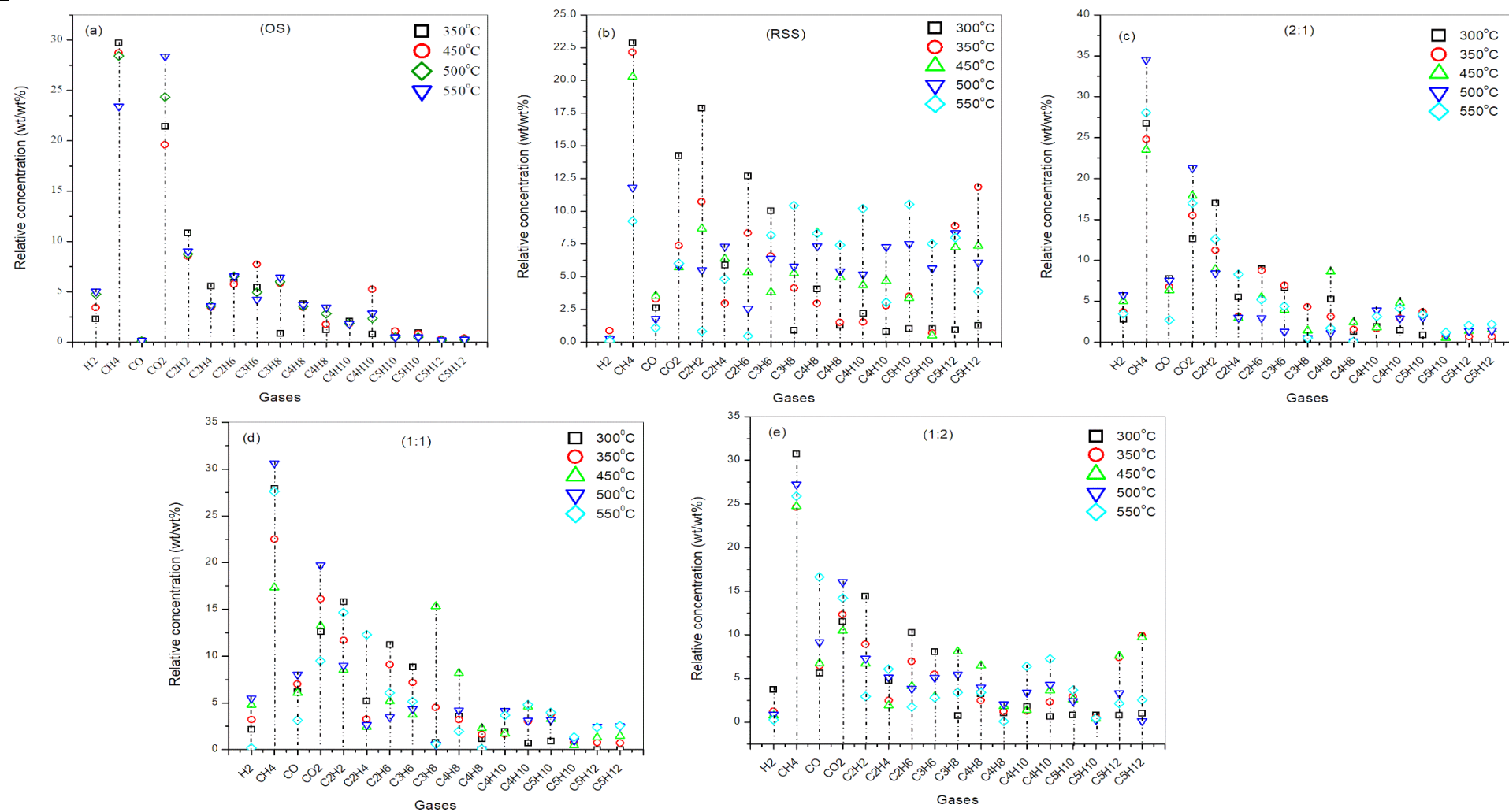


Fig 6.9. Relative concentrations of permanent and hydrocarbon gases produced during co-pyrolysis experiments at a heating rate of 5°C/min, pyrolysis temperature of 550°C for (a) OS, (b) RSS, and at blending ratio of (c) 1:2, (d) 1:1, and (e) 2:1.

Table 6.10. Relative concentration of produced hydrocarbon and permanent gases obtained during individual pyrolysis of OS and RSS and co-pyrolysis experiments in blending ratio of 1:2, 1:1, and 2:1 at heating rate of 5°C/min.

Blending ratio (%)	Pyrolysis Temperature (°C)	H ₂ (%)	CH ₄ (%)	CO (%)	CO ₂ (%)	C ₂ H ₂ (%)	C ₂ H ₄ (%)	C ₂ H ₆ (%)	C ₃ H ₆ (%)	C ₃ H ₈ (%)	C ₄ H ₈ (iso)(%)	C ₄ H ₈ (n) (%)	C ₄ H ₁₀ (iso) (%)	C ₄ H ₁₀ (n) (%)	C ₅ H ₁₀ (iso)(%)	C ₅ H ₁₀ (n)(%)	C ₅ H ₁₂ (iso)(%)	C ₅ H ₁₂ (n)(%)
OS[72]	300	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	350	2.29	29.72	0.14	21.42	10.84	5.54	5.96	5.43	0.85	3.81	1.22	2.07	0.77	0.97	0.95	0.00	0.00
	450	3.44	28.69	0.03	19.61	8.55	3.48	5.76	7.71	5.82	3.46	1.74	1.81	5.25	1.09	0.82	0.28	0.38
	500	4.75	28.40	0.10	24.36	8.75	3.60	6.56	4.97	6.00	3.55	2.81	1.85	2.37	0.49	0.51	0.19	0.27
	550	5.05	23.40	0.14	28.36	9.03	3.60	6.53	4.20	6.41	3.70	3.43	1.82	2.87	0.49	0.51	0.19	0.27
RSS	300	2.80	26.74	7.76	12.63	17.00	5.51	8.92	6.65	0.40	5.27	1.28	1.86	1.43	0.87	0.87	0.00	0.00
	350	3.70	24.78	6.73	15.50	11.24	3.11	8.74	6.91	4.32	3.10	1.56	1.62	2.91	3.67	0.71	0.70	0.70
	450	4.99	23.54	6.36	17.91	8.93	2.93	5.49	3.93	1.41	8.61	2.41	1.80	4.81	3.45	0.50	1.37	1.55
	500	5.76	34.50	7.55	21.30	8.44	3.01	2.95	1.28	0.51	1.12	0.07	3.91	2.91	2.98	0.91	1.37	1.42
	550	3.46	28.07	2.69	16.97	12.58	8.31	5.18	4.39	0.49	1.70	0.07	3.15	4.12	3.39	1.17	2.04	2.20
1:2	300	2.16	27.92	6.18	12.61	15.82	5.21	11.24	8.86	0.80	3.58	1.14	1.94	0.72	0.91	0.91	0.00	0.00
	350	3.20	22.51	6.99	16.11	11.68	3.23	9.08	7.18	4.48	3.22	1.62	1.68	3.02	3.81	0.74	0.73	0.72
	450	4.76	17.34	6.06	13.24	8.51	2.45	5.21	3.74	15.35	8.20	2.29	1.72	4.59	3.28	0.48	1.31	1.48
	500	5.49	30.62	8.03	19.72	8.97	2.63	3.49	4.36	0.54	4.19	0.07	4.15	3.10	3.17	0.97	2.46	2.51
	550	0.18	27.62	3.14	9.51	14.69	12.27	6.05	5.13	0.58	1.99	0.08	3.68	4.81	3.96	1.36	2.38	2.57

1:1	300	3.72	30.72	5.63	11.50	14.43	4.75	10.25	8.08	0.73	3.26	1.04	1.77	0.66	0.83	0.83	0.76	1.02
	350	1.21	24.65	6.44	12.33	8.94	2.48	6.95	5.49	3.43	2.46	1.24	1.29	2.31	2.92	0.57	7.40	9.89
	450	0.74	24.72	6.76	10.45	6.71	1.93	4.11	2.95	8.09	6.47	1.81	1.36	3.62	2.59	0.38	7.62	9.70
	500	0.88	27.24	9.16	16.06	7.31	5.15	3.85	5.11	5.44	3.97	2.06	3.38	4.31	2.39	0.28	3.29	0.12
	550	0.27	25.91	16.65	14.22	2.97	6.09	1.76	2.83	3.40	3.39	0.08	6.39	7.25	3.66	0.45	2.14	2.55
2:1	300	0.26	22.85	2.63	14.25	17.88	5.89	12.70	10.02	0.90	4.05	1.29	2.19	0.82	1.03	1.03	0.94	1.27
	350	0.86	22.13	3.28	7.37	10.71	2.97	8.33	6.58	4.11	2.95	1.49	1.54	2.77	3.50	0.68	8.87	11.85
	450	0.18	20.29	3.55	5.72	8.68	6.39	5.32	3.82	5.26	8.37	4.94	4.35	4.68	3.35	0.49	7.25	7.36
	500	0.26	11.82	1.78	5.84	5.50	7.31	2.56	6.37	5.77	7.32	5.43	5.19	7.28	7.52	5.62	8.34	6.08
	550	0.07	9.23	1.09	6.02	0.82	4.84	0.48	8.17	10.44	8.32	7.41	10.20	3.05	10.51	7.51	7.98	3.87

6.4.3. Gas chromatography and Mass spectrometry (GC-MS)

GC-MS analysis was performed to identify the distribution of different compounds present in the co-pyrolytic oil samples. Quantification of the GC-MS analysis of the pyrolytic oil sample obtained at optimum condition (blending ratio of 1:1, 550°C, at 5°C/min) is summarized in Table 6.11. Quantification of identified compounds for oil samples obtained from blending ratios of 2:1 and 1:2 are provided in Table 6.12 and 6.13, respectively. The spectra for each blending ratio and oil obtained from individual pyrolysis of OS and RSS in Fig 6.10 (a-e). The quantification of the identified compounds as per their functional groups at each blending ratio and for individual pyrolysis of OS and RSS is summarized in Table 6.14. The co-pyrolysis pyrolytic oil obtained at the different blending ratios discussed previously ranged from carbon number C₆ to C₂₂, and molecular weight of 83 to 369. Chen et al. [96], reported similar findings for co-pyrolysis of oil shale and wheat straw, for carbon number in pyrolytic oil samples to range from C₆ to C₂₁. The GC-MS analysis of oil obtained from OS sample showed the occurrence of carbon number from C₆ to C₃₈ [22, 72], and the oil obtained from RSS sample showed carbon number distribution from C₂ to C₁₆ [245]. The oil obtained from OS sample showed 50.29 wt/wt% aliphatics, 28.66 wt/wt% aromatics, 18.72 wt/wt% oxygenated compounds, and 2.05 wt/wt% sulfur compounds [22]. On the other hand, the composition of the oil obtained from pyrolysis of RSS sample showed abundance of oxygenated compounds with 27 wt/wt% phenolic compounds, 13 wt/wt% organic acids, 16.5 wt/wt% cresols, 12.8 wt/wt% aromatics and 26.5 wt/wt% heteroatomic compounds [245]. The pyrolytic oil obtained at optimum pyrolysis condition (blending ratio 1:1, heating rate of 5°C/min, and pyrolysis temperature of 550°C) showed the area percentage of aliphatic compounds to be 28.41 wt/wt%, 41 wt/wt% of oxygenated compounds, 30 wt/wt% aromatic compounds, and 0.57 wt/wt% sulfur compounds. At OS:RSS blending ratio of 1:2, the obtained pyrolytic oil showed 19.25 wt/wt% aliphatics, 45 wt/wt% oxygenated compounds, 38% aromatics, and 1.25 wt/wt% sulfur

compounds. Increasing the concentration of oil shale at the blending ratio to 2:1, showed an increase in the concentration of aliphatics to 31.15 wt/wt% and decreased the percentage of oxygenated compounds and aromatic compounds to 32 wt/wt%, and 35 wt/wt% respectively. The concentration of sulfur compounds increased to 1.75 wt/wt%. The concentration of sulfur compounds was found to be the highest at oil shale to rubber seed shell blending ratio of 2:1, and lowest at blending ratio of 1:1. The pyrolytic oils obtained from pyrolysis of rubber seed shell showed a dominance of acetic acid, phenolic compounds, with a small concentration of aromatic compounds. The decrease in the percentage of oxygenated compounds in the pyrolytic oil with increase in concentration of oil shale in the blend have been reported in previous studies [87, 96, 254]. The inherent minerals in the oil shale sample tend to have a catalytic effect on the hydrocarbon vapors produced during the volatilization of lignocellulosic biomass [255]. The presence of silica minerals in oil shale inhibits the cracking of aliphatic compounds and reduces the formation of oxygenated compounds in oil shale pyrolysis [126]. The decrease in the percentage of oxygenated compounds in the co-pyrolysis oil sample occurred due to the interaction of kerogen and free radicals produced during biomass cracking, leading to a higher percentage of aliphatic compounds [96, 256].

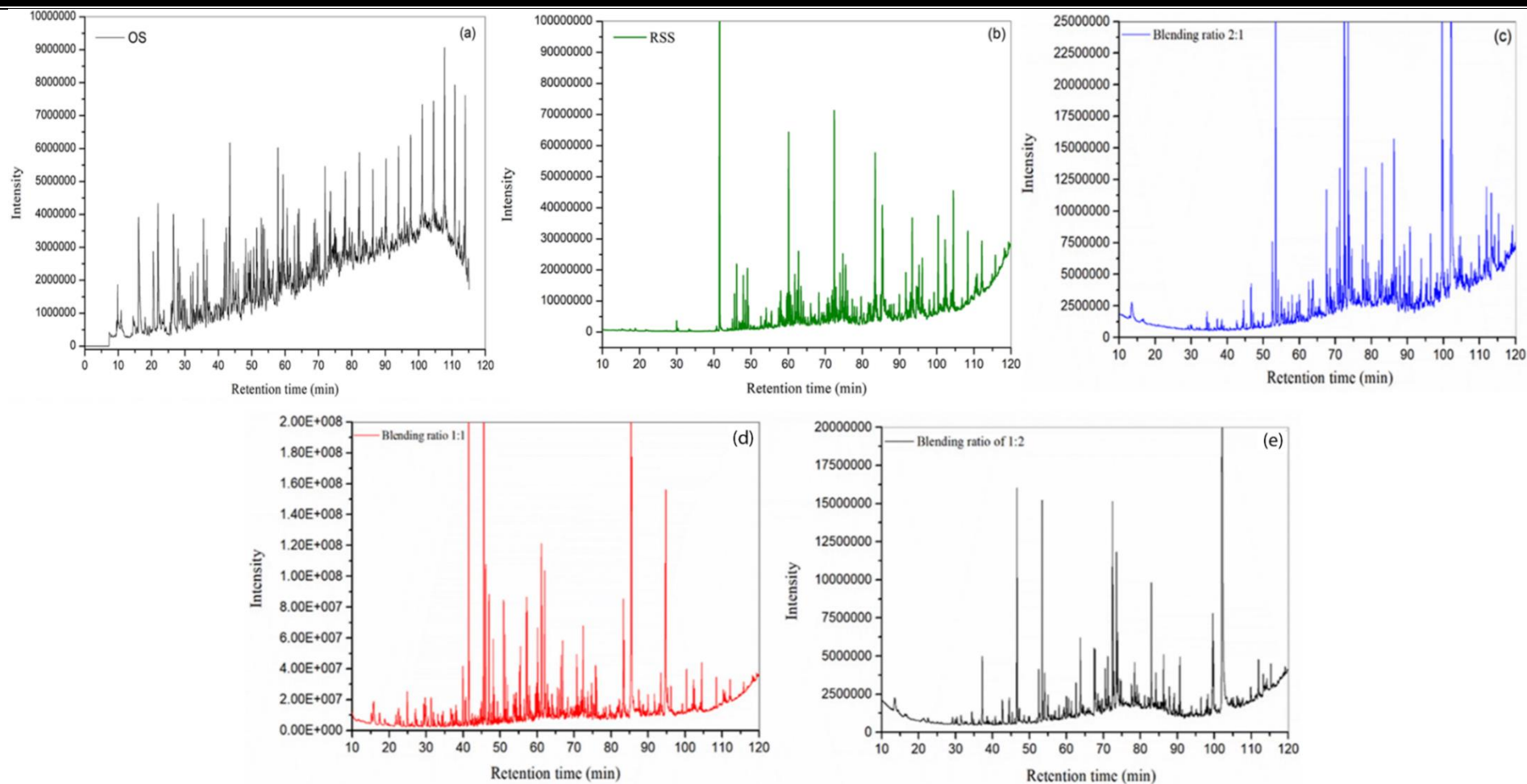


Fig 6.10. GC spectra of GC-MS analysis of oil sample obtained at temperature of 550°C and heating rate of 5°C/min for oil obtained from (a) oil shale, (b) rubber seed shell, and oil shale to rubber seed shell blend ratio of (c) 1:1, (d) 1:2, and (e) 2:1.

Table 6.11. The relative concentration of identified compounds during co-pyrolysis experiments at blending ratio of 1:1 at a heating rate of 5°C/min and 550°C.

Compound	Retention time (min)	Molecular weight (mol/g)	Relative Area (%)
Toluene	12.8	92.14	4.62
Benzene, 1,3 dimethyl	39.74	148.24	0.57
Benzenepropanal	44.38	148.2	0.46
Benzene, (2-methylpropyl)	45.47	134.22	20.29
1,2-benzenedicarboxylic acid, diheptyl ester	47.99	362.5	0.93
2methylpentane	49.56	86.18	2.21
Hydrazine, phenyl	50.26	108.14	0.57
2,3 dimethylbutane	52.56	86.17	0.32
Benzene, N-butyl	57.39	213.3	2.13
2,4-Di-tert-butylphenol	61.11	206.32	19.22
Benzocycloheptatetraene	63.41	214.22	0.98
Benzaldehyde	65.24	106.12	0.24
o-xylene	67.02	106.16	0.79
Anthracene, 2-methyl-	69.25	192.25	1.36
phenol, 2,3,5,6-tetramethyl	72.13	150.22	2.02
Heptadecane	73.55	240.47	7.45
3-methyl, nonane	75.41	142.28	1.67
3-ethyl, tetradecane	77.37	226.44	0.41
alpha, dichloro methyl ether	79.56	114.96	0.82
Benzene, 1-methyl, 2-nitro	82.38	151.16	2.54
10-methylnonadecane	83.1	282.5	1.23
Dodecane	85.14	170.33	2.46
1-Tridecanamine	87.39	199.38	4.40
Napthalene	88.45	128.17	0.41
1,2-benzenedicarboxylic acid, butyl cyclohexyl ester	90.32	304.4	0.49
Sulfurous Acid, hexyl pentadecyl ester	92.85	376.6	0.57

pentadecylamine	94.19	227.43	0.32
Pentanoic acid, 2-methylpropyl ester	96.44	158.24	0.38
Hexylene glycol	98.43	118.17	0.54
Benzocycloheptatetraene	100	214.22	7.34
2-ethyl, 1-dodecanol	103.15	214.39	2.13
9,10-anthracenedione	104.16	239.23	0.62
1,2-benzenedicarboxylic acid, monobutyl ester	108.42	222.24	6.76
4, methyl dodecane	110.24	184.36	2.13
Benzocycloheptatetraene	112.4	214.22	0.43

Table 6.12. Relative concentration of identified compounds during co-pyrolysis experiments at blending ratio of 1:2 at heating rate of 5°C/min and 550°C.

Compound	Retention time (min)	Molecular Weight (mol/g)	Relative Area (%)
Toluene	12.89	92.14	1.65
p-xylene	15.79	106.16	3.36
benzene, 1, 3-dimethyl	17.35	148.24	0.78
benzene, 1-ethyl, 3-methyl	22.68	120.19	4.38
mesitylene	28.57	120.19	0.57
p-xylene	29.57	106.16	5.82
Ethanol, 2-(phenylamino-)	31.38	137.18	0.24
di-t-butylacetylene	39.97	138.25	1.43
1,2 benzenedicarboxaldehyde	41.20	134.13	0.24
1,2-Benzenedicarboxylic acid, diheptyl ester	45.02	362.50	16.87
benzeneacetaldehyde	45.55	120.15	0.37
Toluene	46.07	92.14	0.14
4(1H)-Pyrimidinone, 2,3-dihydro-5-methyl-2-thioxo-	46.98	142.18	0.48
Leucinocaine	48.15	292.40	0.63
Aniline	50.88	93.13	1.27

p-xylene	53.74	106.16	1.35
Acetic acid, [(4-methylphenyl)sulfonyl]-, ethyl ester	55.43	242.29	0.41
Ethyl benzene	57.12	106.17	3.14
Trichloromethane	60.12	119.38	3.64
Hexane 3, ethyl	60.12	114.23	2.36
1,2-Benzenediol, 3-methyl	61.15	124.02	9.89
p-xylene	62.05	106.16	8.98
diphenyl ether	63.10	170.20	0.85
benzaldehyde	66.99	106.12	0.62
Acetic acid, [(4-methylphenyl)sulfonyl]-, ethyl ester	72.59	242.29	4.33
benzaldehyde	75.84	106.12	1.07
Pentanoic acid, 2-methylpropyl ether	83.51	286.41	4.80
Benzidine	85.58	184.24	11.95
Benzene, (2-methylpropyl-)	100.00	134.22	2.60
Pentanoic acid, 2 methylpropyl ester	102.48	158.24	2.38
1-tridecanamine	104.55	257.45	3.40

Table 6.13. Relative concentration of identified compounds during co-pyrolysis experiments at blending ratio of 2:1 at heating rate of 5°C/min and 550°C.

Compound	Retention Time (min)	Molecular Weight (mol/g)	Relative area (%)
Toluene	10.00	92.14	0.61
Benzene, 1,3 dimethyl	15.25	148.24	2.91
Benzenepropanal	41.64	134.17	30.88
Benzene, (2-methylpropyl)	45.48	134.22	23.68
1,2-benzenedicarboxylic acid, diheptyl ester	45.61	362.50	0.11
2, methylpentane	47.56	86.12	0.13
Hydrazine, phenyl	50.86	108.14	2.61
2,3 dimethylbutane	52.56	86.17	0.13
Benzene, N-butyl	54.40	134.22	0.86

2,4-Di-tert-butylphenol	57.11	206.32	3.75
Ethyl benzene	59.12	106.17	1.18
Hexane 3, ethyl	60.12	114.23	0.88
Benzaldehyde	61.24	106.12	3.15
o-xylene	62.02	106.16	1.75
phenol, 2,3,5,6-tetramethyl	62.14	150.22	0.12
3-methyl, nonane	65.71	142.28	0.53
alpha, dichloro methyl ether	69.56	114.96	0.16
3-ethyl, tetradecane	72.37	226.44	0.05
Benzene, 1-methyl, 2-nitro	75.38	151.16	2.29
Dodecane	77.84	170.33	1.57
1-Tridecanamine	83.39	199.38	1.94
1,2-benzenedicarboxylic acid, butyl cyclohexyl ester	85.32	304.40	8.15
Napthalene	88.45	128.17	4.03
pentadecylamine	94.80	227.43	1.80
Pentanoic acid, 2-methylpropyl ester	98.45	158.24	0.08
2-ethyl, 1-dodecanol	103.15	214.39	0.65
Hexylene glycol	100.44	118.17	1.25
Trichloromethane	102.00	119.38	1.07
9,10-anthracenedione	104.66	208.21	1.51
1,2-benzenedicarboxylic acid, monobutyl ester	110.42	222.23	1.51
dodecane	112.24	170.33	0.68

Table 6.14. Composition of oil samples obtained from pyrolysis of OS and RSS individually, and during co-pyrolysis experiments at OS to RSS blending ratio of 1:1, 2:1, and 1:2 respectively at a heating rate of 5°C/min and 550°C.

Functional groups	Relative concentration (wt/wt%)				
	OS[22]	RSS[245]	1:1	2:1	1:2
Aromatics	28.66	12.8	30	35	38
Saturated aliphatics	38.29	---	14	18	10
Unsaturated aliphatics	12	---	14.41	13.15	9.25
Oxygenated compounds	18.72	56.5	41	32.1	41.42
Sulfur compounds	2.06	0.00	0.57	1.75	1.25

6.4.4. Nuclear magnetic resonance (^1H NMR) spectroscopy analysis

NMR (^1H) spectroscopy of the oil sampled obtained at 5°C/min and 550°C at blending ratios of 1:2, 1:1, and 2:1 are shown in Fig 6.11. The quantification of different functional groups is tabulated in Table 6.15. The pyrolytic oil obtained from OS to RSS at blend ratio of 1:2, showed high percentage of aliphatic α -heteroatoms and unsaturation of 36.25% compared to 34% and 25.30% at blending ratio of 1:1 and 2:1, respectively. It may be noted that, the oil produced from individual pyrolysis of OS and RSS showed a concentration of 29% and 25.3%, respectively of aliphatic α -heteroatoms and unsaturation. It was observed that with an increase in the percentage of oil shale in the blend, the concentration of aliphatic compounds increased from 21.99% to 25.50% and 30.20% at, blending ratio of 1:2, 1:1, and 2:1, respectively. Oil samples obtained from individual pyrolysis of OS and RSS showed 36% and 20% aliphatic compounds, respectively (Table 7). The concentration of aromatic compounds decreased from 16.68% for blending ratio of 1:2 to 10.45% at blending ratio of 1:1, but increased to 20.40% for blending ratio of 2:1 as compared to 21% and 31.4% of aromatics in oil produced from OS

and RSS, respectively. The oil produced from pyrolysis of RSS showed 15.7% of methoxy and carbohydrates, as compared to 3% in the oil produced from pyrolysis of OS. The concentration of α -Methylene to aromatic was found to be 21.01%, 17.02%, and 15.45% at blending ratio of 1:1, 1:2, and 2:1 respectively. For pyrolysis of OS and RSS, the concentration of α -Methylene to aromatic was seen to be 10% and 4.6%, respectively. It was observed that, for co-pyrolysis of oil shale (OS) and rubber seed shell (RSS), the concentration of methoxy compounds was recorded to be 7.66%, 8.55%, and 10.65% at blending ratio from 1:2, 1:1, and 2:1 respectively. The lower percentage of methoxy compounds in the co-pyrolytic oil samples was also observed in FTIR-ATR analysis (Section 3.5.1). Previous studies on NMR analysis of pyrolytic oil derived from rubber seed shell (RSS) showed 32% of methoxy compounds[245]. The production of -OH and -H free radicals from valorization of biomass is absorbed by kerogen, leading to generation of higher concentration of aliphatic compounds[87]. This explains the increase in the concentration of aliphatic compounds in the co-pyrolytic oil sample. Co-pyrolysis of rubber seed shell with oil shale showed the catalytic effect of oil shale on the reduction in the concentration of methoxy compounds with an increase in aliphatic compounds. This will increase the heating value of co-pyrolytic oil because of the decrease in the concentration of oxygenated compounds.

Table 6.15. Concentration of functional groups identified by ^1H NMR of pyrolytic oils obtained from OS and RSS individually, and from co-pyrolysis experiments at blending ratio of 1:2, 1:1, and 2:1 at 550°C and 5°C/min.

Proton Assignment (^1H)	Chemical Shift, ppm	OS (%) [22]	RSS (%)	1:2 (%)	1:1 (%)	2:1 (%)
Alkanes	0.5-1.5	36	20	21.99	25.50	30.20
Aliphatics α -heteroatoms or unsaturations	1.5-3	29	25.3	36.25	34	25.30
α -Methylene to aromatic	3-4.5	10	4.6	17.02	21.01	15.45
Methoxys and carbohydrates	4.5-6	3	15.7	7.66	8.55	10.65
Aromatic	6-8.5	21	31.4	16.68	10.45	20.40
Esters and carboxylic acids	8.5-10	1	3	0.40	0.44	1

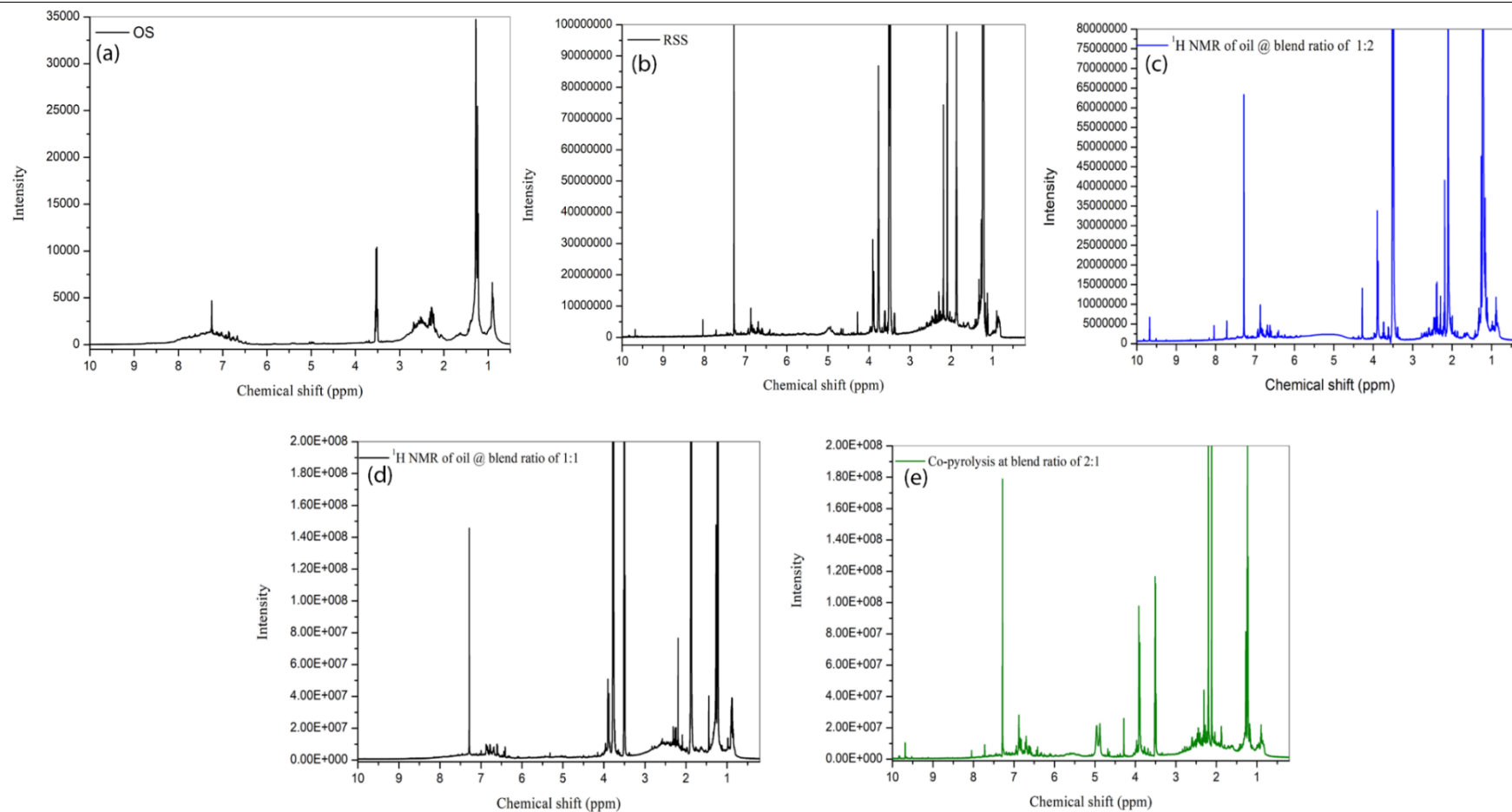


Fig 6.11. ^1H NMR of co-pyrolytic oil obtained from the pyrolysis of (a) OS, (b) RSS, and blend in ratio of (c) 1:2, (d) 1:1 and (e) 2:1 at temperature of 550°C and heating rate of $5^\circ\text{C}/\text{min}$.

6.5. Conclusive summary

Co-pyrolysis of oil shale and rubber seed shell at different blending ratios showed the catalytic effect of oil shale on the oil produced from rubber seed shell. Kinetic study of co-pyrolysis process showed mean apparent activation energies to be 249.5 kJmol^{-1} , 270 kJmol^{-1} , and 275 kJmol^{-1} at blending ratios of 1:2, 1:1, and 2:1, respectively. Occurrence of F2 second order reaction model and A3 Avrami Eroffev nucleation model was observed in blending ratio of 1:2 and 1:1. However, at blending ratio of 2:1, D3 diffusion model occurred as an intermediate reaction model between F2 and A3 reaction model. Optimization of lab-scale co-pyrolysis parameters were performed to maximize the oil yield and minimize the yields of gas and aqueous phases. The blending ratio of 1:1, heating rate of $5^{\circ}\text{C}/\text{min}$, and pyrolysis temperature of 550°C were found to be the most suitable conditions for optimum oil yield. The optimization model predicted maximum mass loss of 44.9 wt% oil yield of 28.5 wt/wt%, gas yield of 10.9 wt/wt%, aqueous phase of 8.25 wt/wt%, and char yield of 52.35 wt/wt% with model confirmation of 97%. GC analysis of pyrolytic gases showed that with the increase in blend ratio (more oil shale), the percentage of $\text{C}_3\text{-C}_5$ gases increases. GC-MS analysis showed the carbon number of the produced oil samples to be in the range of C_6 to C_{22} . FTIR, GC-MS, and ^1H NMR analyses of co-pyrolytic oil sample showed a decrease in the percentage of oxygenated compounds and increased the concentration of aliphatic compounds with an increase in the percentage of oil shale in the blend. The aliphatic content in the pyrolytic oil increased from 19.2 % to 31.15%, and $-\text{OH}$ percentage decreased from 41.42% to 32.1%. The optimum oil yield showed a composition of 28.41% aliphatics, 41% $-\text{OH}$ compounds, and 30% aromatics. This indicates that the co-pyrolysis of rubber seed shell with Indian oil shale led to increase in the grade of the pyrolytic oil, therefore increasing the potential of the obtained pyrolytic oil to be used as a valuable source of alternate high-value fuel.

Chapter 7

Conclusion and future work



7. Conclusion

Physicochemical and thermochemical characterization of Indian oil shale showed the oil shale sample to be of siliceous type with total organic matter content of 21 wt%. Kerogen extracted from Indian oil shale by acid-solvent demineralization process was identified to be of type-II using Rock-Eval analysis. Kinetics study of the pyrolysis process of the oil shale sample showed the mean apparent activation energy values in the range of 230 to 245.6 kJmol⁻¹. Kinetic study of the pyrolysis of kerogen estimated mean apparent activation energy values in the range of 219 to 236 kJmol⁻¹. Oil shale degradation process showed the occurrence of two reaction model, viz. D3 Diffusion and A2 Avrami Eroffev reaction model. And, the entire kerogen degradation process followed two reaction models viz. F1 first-order reaction model followed by A2 Avrami Eroffev nucleation reaction of produced hydrocarbons. The overall kinetic study demonstrated the swelling of kerogen, followed by breakdown for generation of hydrocarbons and eventual nucleation of the produced hydrocarbons. TG-FTIR analysis showed the generation of hydrocarbons from kerogen begins around 200°C, compared to 300°C for oil shale samples. TGA-FTIR analysis helps in simultaneous identification of the evolved products during oil shale pyrolysis. The evolved gases showed presence of CH₄, CO₂, aliphatic C-H, aromatic C-H and sulfur oxide functional groups. Comparison of TG-FTIR analysis of extracted kerogen and oil shale pyrolysis showed the occurrence of cracking and coking reaction due to the delay in vaporization temperature of hydrocarbons in the presence of inherent minerals. RSM optimization of lab-scale pyrolysis studies of the Indian oil shale sample showed that maximum oil yield was obtained at pyrolysis temperature of 600°C at a heating rate of 10°C/min for particle size of 150 micron. An optimum mass conversion of 27.65 wt%, with 14.56 wt% oil yield, 9.12 wt% gas yield, 2.97 wt% aqueous phase and 72.35 wt% of spent shale were observed. Characterization of the produced oil sample

by GC-MS and ^1H NMR analysis showed mean 58.13% and aromatic 24.83%. ^1H NMR analysis of oil obtained from pyrolysis of kerogen, oil shale, and solvent extracted bitumen showed cracking and coking of produced hydrocarbons due to catalytic effect of minerals during simultaneous degradation of kerogen and mineral matter in oil shale. Higher percentage of aliphatic compounds in the shale oil reveals that it possesses higher energy density and can be considered as a potential source alternate to crude oil.

During High-pressure pyrolysis, kinetic study showed the average activation energy to increase from $247.56 \text{ kJmol}^{-1}$ at 1 bar to 434, 443, and 451 kJmol^{-1} at 5, 10, and 20 bar respectively, but reduced to 341 kJmol^{-1} at 30 bar. High-pressure kinetics showed the occurrence of three-reaction model, D3 diffusion at low conversions, F2 second order reaction at intermediate conversions and A3 Avrami Eroffev model at higher conversions. The effect of vaporization of oil due to cracking and the occurrence of secondary reactions were observed with the decrease of oil yield and an increase in gas yield with an increase in pyrolysis pressure. GC analysis of the pyrolytic gas samples showed that the relative concentration of $\text{C}_2\text{-C}_4$ gases obtained at high pressure increased dramatically compared to atmospheric pressure. SimDist analysis showed the increase of lighter and middle fractions from 26.2 wt/wt% and 18.3 wt/wt% at 1 bar to 45.3wt/wt % and 47.2 wt/wt% at 30 bar respectively categorizing in the gas-oil and kerosene section of distillates. FTIR and ^1H NMR analysis showed a significant decrease in the concentration of aldehydes, ketones, carboxylic acids, and aromatics and an increase in concentration of alkanes at high pressure. The decrease in the percentage of aromatics occurs due to enhanced cracking and coking reactions at high pressure.

The oil samples obtained from hydrous and soaking pyrolysis of Indian oil shale in DI water and brine solution showed the generation of high concentration of aliphatic compounds. A minute concentration of aromatics was identified in oil samples collected from soaking pyrolysis for

soaking period of 1 and 2 weeks, however the concentration of aromatics increased with increase in soaking time from 2 weeks to 3 and 4 weeks. SimDist analysis of oil obtained from soaking pyrolysis at 400°C in brine solution showed the occurrence of carbon number distribution from C₆ to C₃₈, and oil obtained from soaking in DI water showed carbon number from C₆ to C₃₄. However, the oil samples obtained from hydrous pyrolysis experiments in brine solution and DI water at 400°C showed carbon number distribution from C₈ to C₃₈. GC-MS and ATR analysis showed the concentration of organic acids to increase with increase in pyrolysis temperature from 300°C to 350°C and decreased from 350°C to 400°C. The concentration of organic amides was found to be higher in the presence of brine solution during both Soaking and hydrous pyrolysis. However, in the presence of DI water amides were found to occur in minute concentrations. The yield of sulfur moieties was observed to be higher from hydrous pyrolysis and soaking pyrolysis as compared to anhydrous pyrolysis.

Co-pyrolysis of oil shale and rubber seed shell at different blending ratios showed the catalytic effect of oil shale on the oil produced from rubber seed shell. Kinetic study of the co-pyrolysis process showed mean apparent activation energies to increase from 249.5 kJmol⁻¹ to 275 kJmol⁻¹ with increase in oil shale to rubber seed blending ratios of 1:2 to 2:1. For blending ratio of 1:2 and 1:1, F2 second order reaction model and A3 Avrami Eroffev nucleation model were identified as the probable reaction models. However, at blending ratio of 2:1, D3 diffusion model occurred as an intermediate reaction model between F2 and A3 reaction model. Optimization of lab-scale co-pyrolysis parameters showed that the blending ratio of 1:1, heating rate of 5°C/min, and pyrolysis temperature of 550°C were found to be the most suitable conditions for optimum oil yield. FTIR, GC-MS, and ¹H NMR analyses of co-pyrolytic oil sample showed that the aliphatic content in the pyrolytic oil increased from 19.2 % to 31.15%, and –OH percentage decreased from 41.42% to

32.1%. The optimum oil yield showed a composition of 28.41% aliphatics, 41% -OH compounds, and 30% aromatics at blending ratio of 1:1, heating rate of 5°C/min, and pyrolysis temperature of 550°C. GC analysis of pyrolytic gases showed that with the increase in blend ratio (more oil shale), the percentage of C₃-C₅ gases increases. GC-MS analysis showed the carbon number of the produced oil samples to be in the range of C₆ to C₂₂. Compositional analyses of the co-pyrolytic oil sample showed a decrease in the percentage of oxygenated compounds and increased the concentration of aliphatic compounds with an increase in the percentage of oil shale in the blend. The aliphatic content in the pyrolytic oil increased from 19.2 % to 31.15%, and -OH percentage decreased from 41.42% to 32.1%. The optimum oil yield showed a composition of 28.41% aliphatics, 41% -OH compounds, and 30% aromatics. This indicates that the co-pyrolysis of rubber seed shell with Indian oil shale led to increase in the grade of the pyrolytic oil, therefore increasing the potential of the obtained pyrolytic oil to be used as a valuable source of alternate high-value fuel.

Thus, the present study on the investigation of pyrolysis mechanism of Indian oil shale, showed the oil shale sample to have the potential of utilizing it as a source of alternate fuel. The compositional characterization of the oil samples showed abundance of aliphatic compounds in the pyrolytic oil samples obtained from the oil samples. High-pressure pyrolysis of the oil shale sample produced high value oil with abundance of light and middle distillates. Soaking and hydrous pyrolysis experiments of the sample helped in visualizing the effect of underground aquifer in the oil and gas generation process in the subsurface, and also showed the effect of salinity on the yield and composition of the produced hydrocarbons. Co-pyrolysis of the oil shale sample with waste lignocellulosic biomass showed that the abundance of clay and silica minerals acted as catalyst in inhibiting the generation of oxygenated compounds in the pyrolytic bio-oil produced

from lignocellulosic biomass. Therefore, it can be established that, the Indian oil shale sample has the potential to be used as a source of alternate fuel to sustain the energy demand, and can help understand the maturation of hydrocarbons in the subsurface, and also possesses the properties of a catalyst during co-pyrolysis studies with other carbonaceous materials for upgradation of selected products.



7.1. Future work and recommendations

The study can be further continued by investigating the upgradation of the pyrolytic oil produced from oil shale pyrolysis by in-situ catalytic upgradation, and the obtained oil and gas samples can be tested for their compatibility in internal combustion engines. The oil and gas samples can be treated for the removal of sulfur and nitrogen moieties, to obtain clean and commercial grade fuel of true nature.

- a. Catalytic pyrolysis of the oil shale sample to obtain selective products using different heterogenous catalysts to investigate the effect of catalyst bed temperature, regeneration of catalyst, space time and space velocity of pyrolytic vapors.
- b. Design and development of a scale up pyrolysis process model for sustainable conversion of oil shale and other carbonaceous material at pilot level.
- c. In-situ retorting of oil shale using CMG-STAR simulation and model study.
- d. Utilization of spent shale for carbon dioxide sequestration.

7.2. Additional work

7.2.1. Initial study for Catalytic pyrolysis of Indian oil shale

Investigation of the pyrolysis parameters and kinetics of the Indian oil shale sample under various pyrolysis conditions showed the Indian oil shale sample to be a potential feed stock for the production of high-grade oil and gas as a replacement to conventional petroleum crude and natural gas. The studies reported in this work helps in defining the parameters to establish an upgradation process of the produced pyrolytic oil and gases for industrial application, and pave the pathway to scale-up of the established oil shale pyrolysis process.

For that purpose, a two-stage catalytic pyrolysis reactor unit (section 2.13.4) was designed and developed under the funding of NEWGEN-IEDC startup project grant by Technology Incubation

Centre at IIT Guwahati. This study will act as a stepping stone towards an in-depth catalytical pyrolysis study of the considered oil shale sample and potential scale-up towards design and development of a pilot-scale pyrolysis unit. A few selective experiments were performed in the novel catalytic reactor and the observations and methodologies are summarized below.

7.2.2. Observation of catalytic pyrolysis experiments

The oil shale sample showed a maximum mass loss of 21 wt% experiments at pyrolysis temperature of 600°C, at a heating rate of 10°C/min and holding time of 2 hours. For catalytic to feed ratio of 1:50, at catalyst bed temperature of 500°C the total oil yield was observed to be 5.4 wt% of initial sample weight, and 15.6 wt% was gas yield. Increasing the temperature of the catalyst bed to 550°C, the oil yield decreased to 4 wt% of the initial sample weight, and the gas yield increased to 17 wt% of the initial sample weight. For catalyst to feed ratio of 1:25, the oil yield decreased drastically for both catalyst bed temperature of 500°C and 550°C. At catalyst bed temperature of 500°C the oil and gas yield were calculated to be 4.5 wt%, and 16.5 wt% respectively of the initial sample weight. Increasing the catalyst bed temperature to 550°C, decreased the oil yield to 3 wt%, and increased the gas yield to 18 wt% of the initial sample weight. It may be noted that, no aqueous phase was observed in the liquid or oil sample during the catalytic pyrolysis experiments. The yields of different pyrolytic products are tabulated in Table 7.1.

Table 7.1. Tabulation of yield of pyrolytic products during catalytic pyrolysis of Indian oil shale with Ammonium ZSM-5 and pyrolysis temperature of 600°C, at heating rate of 10°C/min and holding time of 2 hours.

Feed to catalyst ratio	Catalyst temperature (°C)	Pyrolysis Temperature (°C)	Mass loss (wt%)	Oil yield (wt%)	Gas yield (wt%)	Char yield (wt%)
1:50	550	600	21	5.4	15.6	79
	500	600	21	4	17	79

1:25	550	600	21	4.5	16.5	79
	500	600	21	3	18	79

7.2.3. Compositional analysis of catalytic pyrolysis oil and gas samples

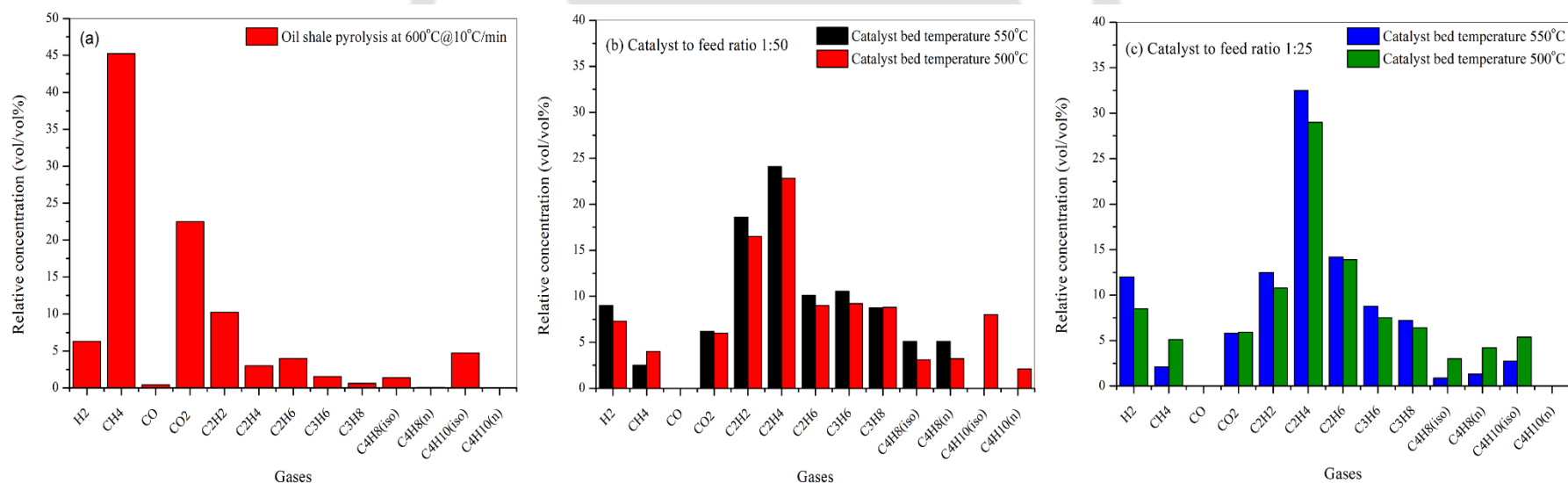
The oil and gas samples obtained during the catalytic pyrolysis experiments were analyzed by GC-SimDist, ^1H NMR analysis, and GC-TCD, FID analysis respectively for the identification of carbon number distribution, and composition of the oil and gas samples.

Gas chromatography

Gas analysis of the oil samples obtained during catalytic pyrolysis showed high concentration of H_2 and C_2 compounds (Table 7.2 and Fig 7.2(a-c)). For catalyst to feed ratio of 1:50, the relative concentration of H_2 was observed to be 9 % and 7.3 % at catalyst bed temperature of 550°C and 500°C respectively. At catalyst to feed ratio of 1:50, the relative concentration of C_2H_4 was observed to be 24.1 %, which increased to 32.5% with increase in catalyst to the feed ratio. At catalyst bed temperature of 500°C, the relative concentration of C_2H_4 was found to be 22.8% and 29% for catalyst to feed ratio of 1:50 and 1:25 respectively. The concentration of C_3 and C_4 gases increased with increase in catalyst bed temperature from 500°C to 550°C for both the cases of the catalyst to feed ratio. For catalyst to feed ratio of 1:50, the relative concentration of C_4H_8 gases changed increased with increase in catalyst bed temperature, however the concentration of C_4H_{10} gases were not observed at catalyst bed temperature of 550°C, but showed minute concentration at 500°C. For catalyst to feed ratio of 1:25, the relative concentration of C_4H_8 and C_4H_{10} gases was observed to be lower at catalyst bed temperature of 550°C, as compared to 500°C. The gas sample obtained during non-catalytic pyrolysis showed the dominant gas to be CH_4 , and CO_2 . However, the relative concentration decreased from C_3 to C_4 gases.

Table 7.2. Mean relative concentration (vol/vol %) of permanent and hydrocarbon gases collected at different catalyst bed temperatures of 550°C and 500°C.

Catalyst to feed ratio	Catalyst temperature (°C)	H ₂ (%)	CH ₄ (%)	CO (%)	CO ₂ (%)	C ₂ H ₂ (%)	C ₂ H ₄ (%)	C ₂ H ₆ (%)	C ₃ H ₆ (%)	C ₃ H ₈ (%)	C ₄ H ₈ (iso) (%)	C ₄ H ₈ (n) (%)	C ₄ H ₁₀ (iso) (%)	C ₄ H ₁₀ (n) (%)	C ₅ H ₁₀ (iso) (%)	C ₅ H ₁₀ (n) (%)	C ₅ H ₁₂ (iso) (%)	C ₅ H ₁₂ (n) (%)
1:50	550	9	2.5	0	6.2	18.6	24.1	10.1	10.54	8.76	5.1	5.1	0	0	0	0	0	0
	500	7.3	4	0	6	16.5	22.8	9	9.2	8.8	3.1	3.2	8	2.1	0	0	0	0
1:25	550	12	2.1	0	5.8	12.47	32.5	14.2	8.77	7.21	0.89	1.31	2.75	0	0	0	0	0
	500	8.5	5.1	0	5.9	10.79	29	13.9	7.5	6.4	3	4.2	5.37	0	0	0	0	0

**Fig 7.1.** Relative concentration of permanent and hydrocarbon gases produced during (a) non-catalytic pyrolysis of oil shale pyrolysis, and catalytic pyrolysis at catalyst to feed ratio of (b) 1:50, and (c) 1:25.

Simulated Distillation of oil sample

Simulated distillation (SimDist) analysis of the oil samples showed the carbon number distribution of C_6 to C_{18} for the oil sample obtained at feed to catalyst ratio of 1:50 and catalyst bed temperature of 550°C , and from C_6 to C_{22} for the oil sample obtained at catalyst bed temperature of 500°C . At catalyst bed temperature of 550°C the oil sample showed 45.2% light, 49.1% middle, and 5.6% heavy distillates. At catalyst bed temperature of 500°C with 44.14% light, 48.91% middle, and 6.47% heavy distillates. With increase in catalyst concentration at the catalyst to feed ratio of 1:25, the carbon number distribution range decreased significantly. At catalyst bed temperature of 550°C and 500°C , the pyrolytic oil sample showed carbon number distribution in the range of C_6 to C_{17} , with 58.65% of light distillates and 41.17% of middle distillates at catalyst bed temperature of 550°C , and 57.93% and 42.05% of light and middle distillates at 500°C , respectively. The pyrolytic oil sample obtained during non-catalytic pyrolysis showed carbon number distribution in the range of C_6 and C_{38} , which summed up to 26.2% light distillates, 18.3% middle distillates, and 55.1% heavy distillates. The distillation curves of the pyrolytic oil samples are shown in Fig 7.3 (a) and (b), and Table 7.3.

Table 7.3. Carbon number distribution as identified by SimDist analysis of pyrolytic oil samples obtained during catalytic pyrolysis at catalyst bed temperature of 550°C and 500°C and comparison with non-catalytic pyrolytic oil.

Carbon number distribution	Non-catalytic[72]	Catalytic pyrolysis			
		1:50 catalyst to feed ratio		1:25 catalyst to feed ratio	
		550°C	500°C	550°C	500°C
C ₆	1.1	7.1	6.93	9.21	9.10
C ₇	2	9.5	9.28	12.33	12.18
C ₈	3	6.4	6.25	8.30	8.20
C ₉	7.1	5.2	5.08	6.75	6.66
C ₁₀	7.1	4.5	4.39	5.84	5.77
C ₁₁	1.3	3.4	3.32	4.41	4.36
C ₁₂	4.3	9.1	8.89	11.81	11.66
C ₁₃	2.7	11.3	11.0	14.66	14.48
C ₁₄	1.2	3.2	3.12	4.15	4.10
C ₁₅	3.5	8.3	8.11	10.77	10.64
C ₁₆	1.7	8.5	8.30	5.03	4.09
C ₁₇	2.2	7.6	7.42	6.76	8.74
C ₁₈	2.7	3.4	3.32	9.21	9.10
C ₁₉	0.3	3.7	4.61	-	-
C ₂₀	3.7	3.1	3.03	-	-
C ₂₁	4.4	3.1	3.03	-	-
C ₂₂	5.4	2.5	3.44	-	-
C ₂₃	3.7	-	-	-	-
C ₂₄	5.8	-	-	-	-
C ₂₅	1.2	-	-	-	-
C ₂₆	2.5	-	-	-	-
C ₂₇	1.6	-	-	-	-
C ₂₈	2.2	-	-	-	-

C ₂₉	1.8	-	-	-	-
C ₃₀	3.6	-	-	-	-
C ₃₁	2.2	-	-	-	-
C ₃₂	2	-	-	-	-
C ₃₃	5.8	-	-	-	-
C ₃₄	4.5	-	-	-	-
C ₃₅	3.2	-	-	-	-
C ₃₆	3	-	-	-	-
C ₃₇	2.2	-	-	-	-
C ₃₈	1	-	-	-	-

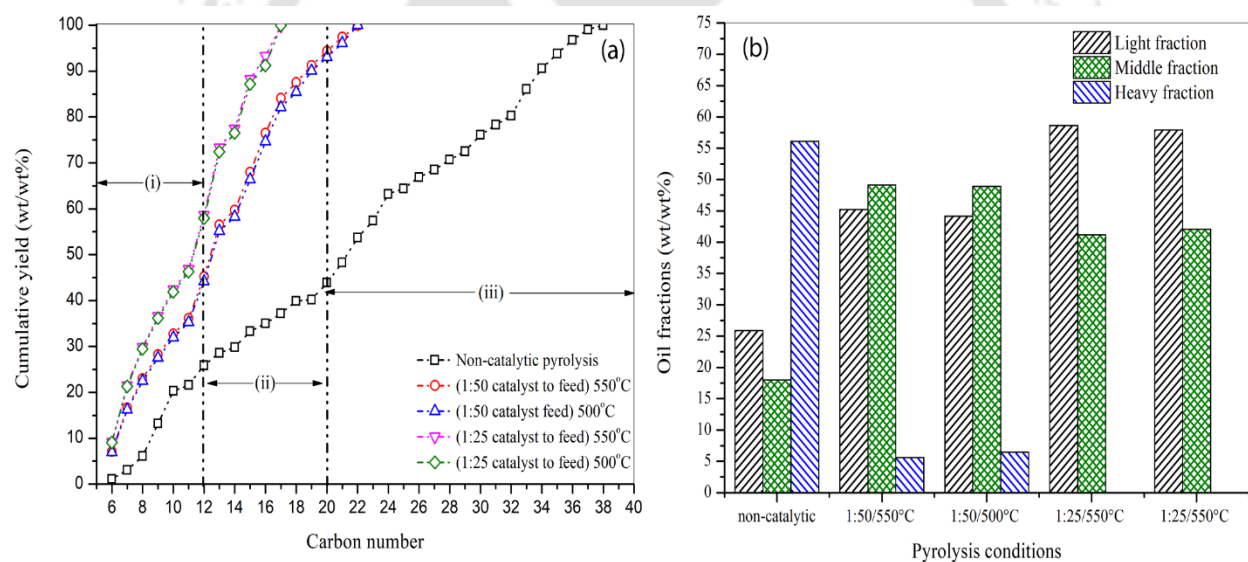


Fig 7.2. (a) Cumulative yield of hydrocarbons based on boiling point of compounds and separated as (i) light, (ii) middle, (iii) heavy fractions or distillations (b) Fractional distribution of light, middle, and heavy distillates at different pyrolysis pressure.

¹H NMR analysis

¹H NMR analysis of the oil samples showed the dominance of aliphatic compounds. The oil sample obtained at feed to catalyst ratio of 1:50 and catalyst bed temperature of 550°C, showed 61% of aliphatics (0.3 to 1.9 ppm), 7% of Aliphatics α -heteroatoms or unsaturation (1.9-3 ppm), 27% of

α -Methylene to aromatics (3 to 4.5 ppm), and 5% Aromatic (6-8.5 ppm). For catalyst temperature of 500°C, the aliphatic content decreased to 58%, with 12% Aliphatics α -heteroatoms or unsaturation, 25% of α -Methylene to aromatics, and 5% of aromatic compounds. For catalyst to feed ratio of 1:25, and catalyst temperature of 550°C, the aliphatic content was recorded to be 65%, with 5% α -heteroatoms and unsaturation, 27% α -Methylene to aromatics, and 3% aromatics. Again, at catalyst bed temperature of 500°C, the oil sample showed 61% of aliphatics, 3% of α -heteroatoms and unsaturation, and 33% α -Methylene to aromatic, and 3% of aromatics. Non-catalytic pyrolysis of the oil shale sample, the integral area showed 36% aliphatics, 29% unsaturated aliphatics and α -heteroatoms. Methoxy and carbohydrates of 10%, 21% of aromatic compounds, and 1% esters and carboxylic acid. The distribution of different functional groups of the pyrolytic oil samples are shown in Table 7.4 and Fig A.5.

Table 7.4. Percentage of compounds determined by ^1H NMR of pyrolytic oil samples obtained during catalytic pyrolysis at catalyst bed temperature of 550°C and 500°C and comparison with non-catalytic pyrolytic oil.

Proton Assignment (^1H)	Non-catalytic [22, 72]	Catalytic pyrolysis			
		1:50 catalyst to feed ratio		1:25 catalyst to feed ratio	
		550°C	500°C	550°C	500°C
Alkanes (0.3-1.9 ppm)	36	61	58	65	61
Aliphatics α -heteroatoms or unsaturations (1.9-3 ppm)	29	7	12	5	3
α -CH ₂ and α -CH ₃ to aromatic (3- 4.5 ppm)	10	27	25	27	33
Methoxys and carbohydrates (4.5- 6 ppm)	3	0	0	0	0
Aromatic (6-8.5 ppm)	21	5	5	3	3
Esters and carboxylic acids (8.5- 10 ppm)	1	0	0	0	0

7.2.4. Conclusive summary

Selective catalytic pyrolysis experiments showed that with increase in the temperature of the catalyst bed and ratio of catalyst to feed ratio significantly affected the yield of the pyrolytic products. Increasing the catalyst bed temperature from 500°C, decreased the oil yield, and increased the gas yield. During catalytic pyrolysis, for both increase in catalyst to feed ratio, and catalyst bed temperature, the concentration of H₂, and C₂ compounds increased dramatically as compared to non-catalytic pyrolysis. ¹H NMR analysis showed that, the concentration of aliphatic compounds increased with increase in catalyst to feed ratio and catalyst bed temperature. For catalyst to feed ratio of 1:50, the obtained oil samples showed the carbon number distribution in the range of C₆ to C₂₂ for both catalyst bed temperature of 500°C and 550°C. At catalyst bed temperature of 550°C the oil sample showed 45.2% light, 49.1% middle, and 5.6% heavy distillates. Similar distribution of distillation fractions was observed at catalyst bed temperature of 500°C with 44.14% light, 48.91% middle, and 6.47% heavy distillates. However, increasing the catalyst to feed ratio to 1:25, the carbon number distribution ranged from C₆ to C₁₇, with 58.65% of light distillates and 41.17% of middle distillates at catalyst bed temperature of 550°C, and 57.93% and 42.05% of light and middle distillates respectively at 500°C.

Further studies are required to be conducted to study the effect of different parameters such as regeneration of catalyst, purge gas flow rate, space time and space velocity in the catalyst reactor on the yield and composition of the produced pyrolytic products.

Publications and Output

Journal Publications from PhD Work:

1. B. Baruah and P. Tiwari, "Investigation of co-pyrolysis mechanism of oil shale and rubber seed shell, product yield and optimization of pyrolysis parameter using Response Surface Methodology", **Fuel**, 317, DOI: 10.1016/j.fuel.2022.123441, 2022.
2. B. Baruah and P. Tiwari, "Compositional and kinetic study of thermal degradation of kerogen using TG-FTIR, NMR, and microscopic study", **AIChE Journal**, Wiley, DOI: 10.1002/aic.17396, 2021.
3. B. Baruah and P. Tiwari, "Effect of High Pressure on Nonisothermal Pyrolysis Kinetics of Oil Shale and Product Yield," **Energy & Fuels**, ACS, 2020/11/18 2020. DOI: 10.1021/acs.energyfuels.0c02538, 2020.
4. B. Baruah and P. Tiwari, "Soaking and hydrous pyrolysis of Indian oil shale: Identification of produced hydrocarbons and moieties", **Fuel**, Elseviers, 322, DOI: 10.1016/j.fuel.2022.124255, 2022.

Other Journal Publications

1. S. Solanki, B. Baruah and P. Tiwari, "Modelling and Simulation of Wood Pyrolysis using COMSOL Multiphysics", **Bioresource Technology Reports**, 17, (2022) 100941, 2022.
2. J. Mathur, B. Baruah, and P. Tiwari, "Optimization of pyrolysis parameters for maximization of bio-oil yield from pyrolysis of lignocellulosic biomass using machine learning algorithms" (*Rebuttal submitted*).
3. B. Baruah, R. Kataki, P. Thakur, and P. Tiwari, "Detailed physicochemical and thermochemical investigation of Upper Assam oil shale," **Journal of Thermal Analysis and Calorimetry**, vol. 138, pp. 1221-1232, 2019. *Springer-Nature*, DOI: 10.1007/s10973-019-08163-2, 2019.
4. B. Baruah, P. Tiwari, P. Thakur, and R. Kataki, "TGA-FTIR analysis of Upper Assam oil shale, optimization of lab-scale pyrolysis process parameters using RSM," **Journal of Analytical and Applied Pyrolysis**, vol. 135, pp. 397-405, 2018. *Elsevier*,

doi.org/10.1016/j.jaap.2018.08.005, 2018.

5. S. Ghosh, B. Baruah, and P. Tiwari, “Investigation of the effect of pressure on pyrolysis kinetics, product yield, and composition during valorization of plastic” (**Under preparation**).

Book chapters:

1. B. Baruah, P. Kalita, L. Pandey, and P. Tiwari, “Petroleum Reservoirs and Oil Production Mechanisms”, *Microbial Enhanced Oil Recovery: Principles and Potential*, Springer Nature, pp 1-21, https://doi.org/10.1007/978-981-16-5465-7_1.

Conferences:

1. B. Baruah and P. Tiwari, “Detailed investigation of pyrolysis mechanism of Indian oil shale”, North East Research Conclave, IIT Guwahati 20th May to 22nd May, 2022 (**Presentation**).
2. B. Baruah and P. Tiwari, “Effect of high-pressure on oil-shale pyrolysis kinetics and product composition”, Research Conclave, IIT Guwahati 22nd to 24th January 2022 (**Presentation**).
3. B. Baruah and P. Tiwari, “Hydrous pyrolysis studies of Indian oil shales in brine solution and de-ionized water”, IICHE-CHEMCON, 27th to 30th December 2021 (**Presentation**).
4. B. Baruah and P. Tiwari, “High-pressure pyrolysis kinetics of Indian oil shale”, ISCRE 26 & APCRE 9, December 2021 (**Poster**).
5. B. Baruah and P. Tiwari, “Investigation of co-pyrolysis mechanism of Indian oil shale and rubber seed shell for production of high value fuel, kinetic study and optimization of pyrolysis parameters”, 10th ICOSSE, AIChE conference, 13-15th September, 2021 (**Presentation**).
6. B. Baruah and P. Tiwari, “Non-isothermal kinetics of co-pyrolysis of Indian oil shale and rubber seed shell, and characterisation of pyrolytic products”, *National Conference on Upstream Petroleum Engineering (NCUPE 2019)*, IIT Guwahati, November 2019 (**Poster**).

7. B. Baruah, and P. Tiwari, "Detailed investigation of pyrolysis kinetics of kerogen and oil shale of North-east India", *Research Conclave 2019, IIT Guwahati, March 2019 (Poster)*.
8. B. Baruah, R. Kataki, P. Thakur, and P. Tiwari, "Detailed physicochemical and thermochemical analyses of Indian oil shale," *ISCRE, Florence, Italy, 2018 (Poster)*.



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Appendix



The supplementary information for different studies reported in the thesis are compiled together in this section and the contents have been mentioned in the text in appropriate positions.

Table A1. Analysis of variance table for the experimental design results of RSM for mass conversion (%).

Source	Sum squares	of Degree of freedom (df)	Mean square	F value	p-value
Model	417.84	9	46.43	19.72	0.0001
A-heating rate	2.98	1	2.98	1.27	0.2929
B-temperature	305.47	1	305.47	129.76	<0.0001
C-particle size	15.52	1	15.52	6.59	0.0333
AB	0.0946	1	0.0946	0.0402	0.8461
BC	0.0021	1	0.0021	0.0009	0.9768
AC	0.4005	1	0.4005	0.1701	0.6908
A ²	5.30	1	5.30	2.25	0.1720
B ²	78.44	1	78.44	33.32	0.0004
C ²	3.68	1	3.68	1.56	0.2464
Residual	18.83	8	2.35		
Lack of fit	18.40	3	6.13	70.44	0.0001
Pure error	0.4353	5	0.0871		
Corrected total	436.67	17			
Standard deviation		1.52	R ²		0.9569
Mean		20.61	Adjusted R ²		0.9421
Coefficient of variation (%)		1.47			

Table A2. Analysis of variance table for the experimental design results of RSM for gas yield (%).

Source	Sum of squares	Degree of freedom (df)	Mean square	F value	p-value
Model	59.93	9	6.66	40.65	<0.0001
A-heating rate	3.54	1	3.54	21.59	0.0017
B-temperature	28.33	1	28.33	172.90	0.0001
C-particle size	4.03	1	4.03	24.57	0.0011
AB	2.16	1	2.16	13.20	0.0067
BC	1.75	1	1.75	10.67	0.0114
AC	1.26	1	1.26	7.72	0.0240
A ²	0.8057	1	0.8057	4.92	0.0574
B ²	13.04	1	13.04	79.56	<0.0001
C ²	0.2453	1	0.2453	1.50	0.2560
Residual	1.31	8	0.1638		
Lack of fit	1.08	3	0.3617	8.01	0.2560
Pure error	0.2258	5	0.0452		
Corrected total	61.25	17			
Standard deviation		0.4048	R ²		0.9786
Mean		9.57	Adjusted R ²		0.9545
Coefficient of variation (%)		4.23			

Table A3. Analysis of variance table for the experimental design results of RSM for aqueous phase (%).

Source	Sum of squares	Degree of freedom (df)	Mean square	F value	p-value
Model	8.47	9	0.9412	4.27	0.0264
A-heating rate	0.7698	1	0.7698	3.49	0.0985
B-temperature	0.2118	1	0.2118	0.9616	0.3555
C-particle size	2.71	1	2.71	12.29	0.0080
AB	0.3121	1	0.3121	1.42	0.2681
BC	0.0002	1	0.0002	0.0009	0.9767
AC	1.23	1	1.23	5.59	0.0456
A ²	1.94	1	1.94	8.79	0.0180
B ²	1.06	1	1.06	4.80	0.0599
C ²	0.0125	1	0.0125	0.0568	0.8176
Residual	1.76	8	0.2203		
Lack of fit	1.61	3	0.5359	17.33	0.0045
Pure error	0.1546	5	0.0309		
Corrected total	10.23	17			
Standard deviation		0.4694	R ²		0.8278
Mean		1.89	Adjusted R ²		0.6340
Coefficient of variation (%)		24.86			

Table A4. Analysis of variance table for the experimental design results of RSM for spent shale (%).

Source	Sum of squares	Degree of freedom (df)	Mean square	F value	p-value
Model	399.96	9	44.44	20.04	0.0001
A-heating rate	2.05	1	2.05	0.9256	0.3642
B-temperature	287.40	1	287.40	129.62	<0.0001
C-particle size	17.93	1	17.93	8.09	0.0217
AB	0.9870	1	0.9870	0.4452	0.5234
BC	0.1128	1	0.1128	0.0509	0.8272
AC	0.0028	1	0.0028	0.0013	0.9725
A ²	4.63	1	4.63	2.09	0.1864
B ²	78.59	1	78.59	35.45	0.0003
C ²	3.13	1	3.13	1.41	0.2688
Residual	17.74	8	2.22		
Lack of fit	17.30	3	5.77	66.25	0.0001
Pure error	0.4353	5	0.0871		
Corrected total	417.69	17			
Standard deviation		1.49	R ²		0.9575
Mean:		79.34	Adjusted R ²		0.9098
Coefficient of variation (%)		1.88			

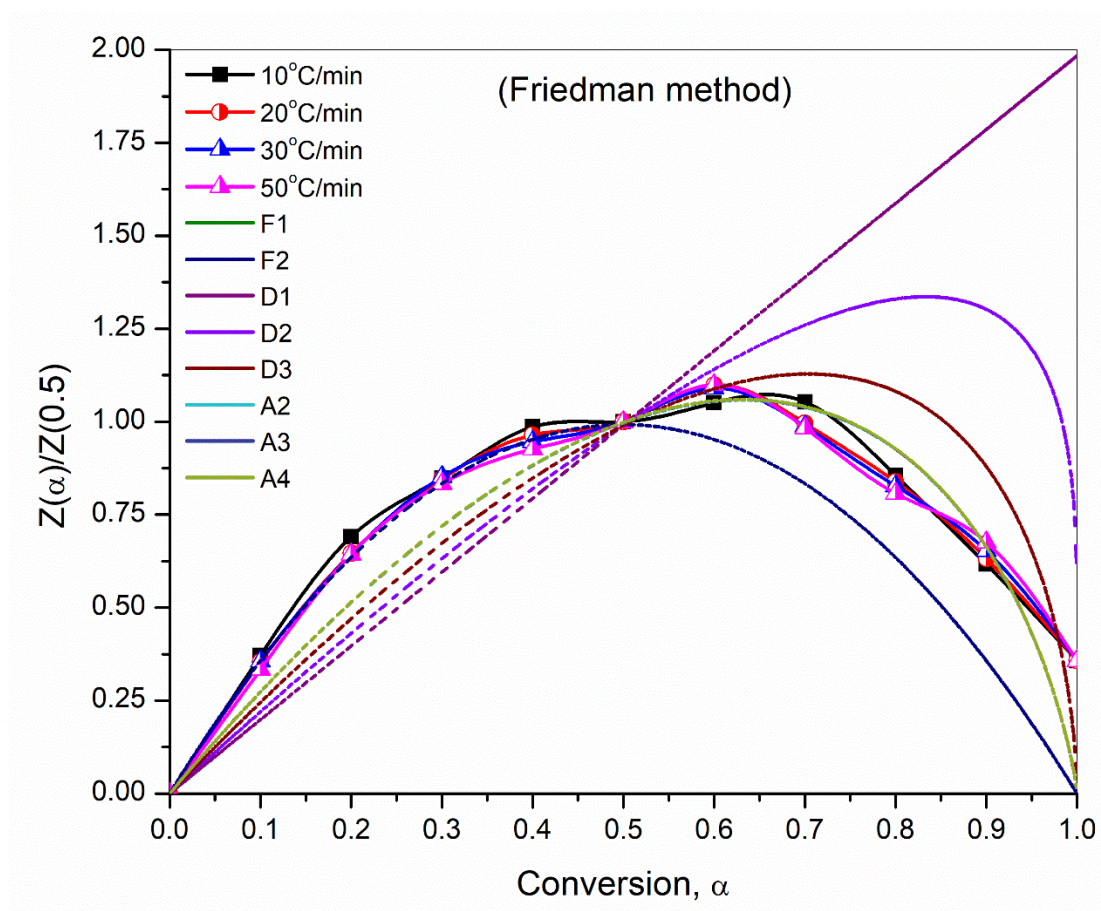


Fig A1. Criado master plot for kerogen degradation using Friedman method.

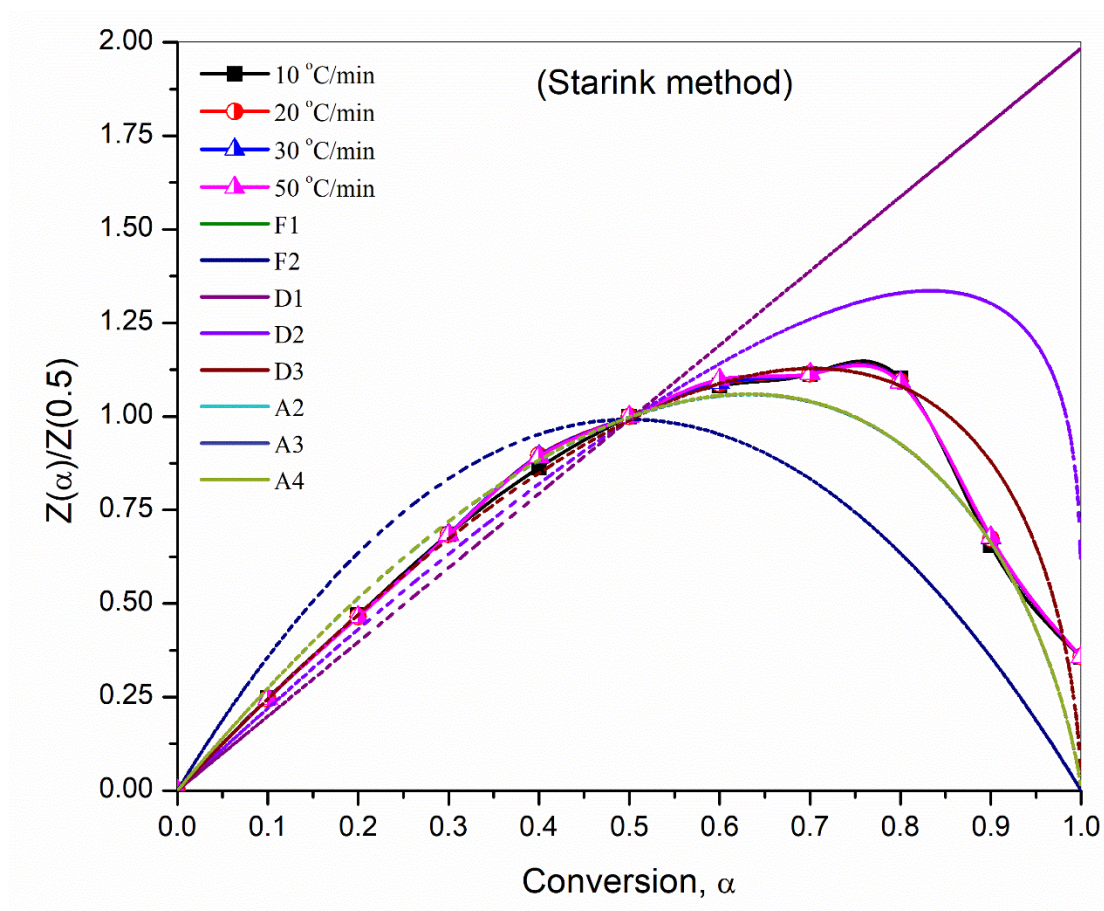


Fig A2. Criado master plot for kerogen degradation using Starink method.

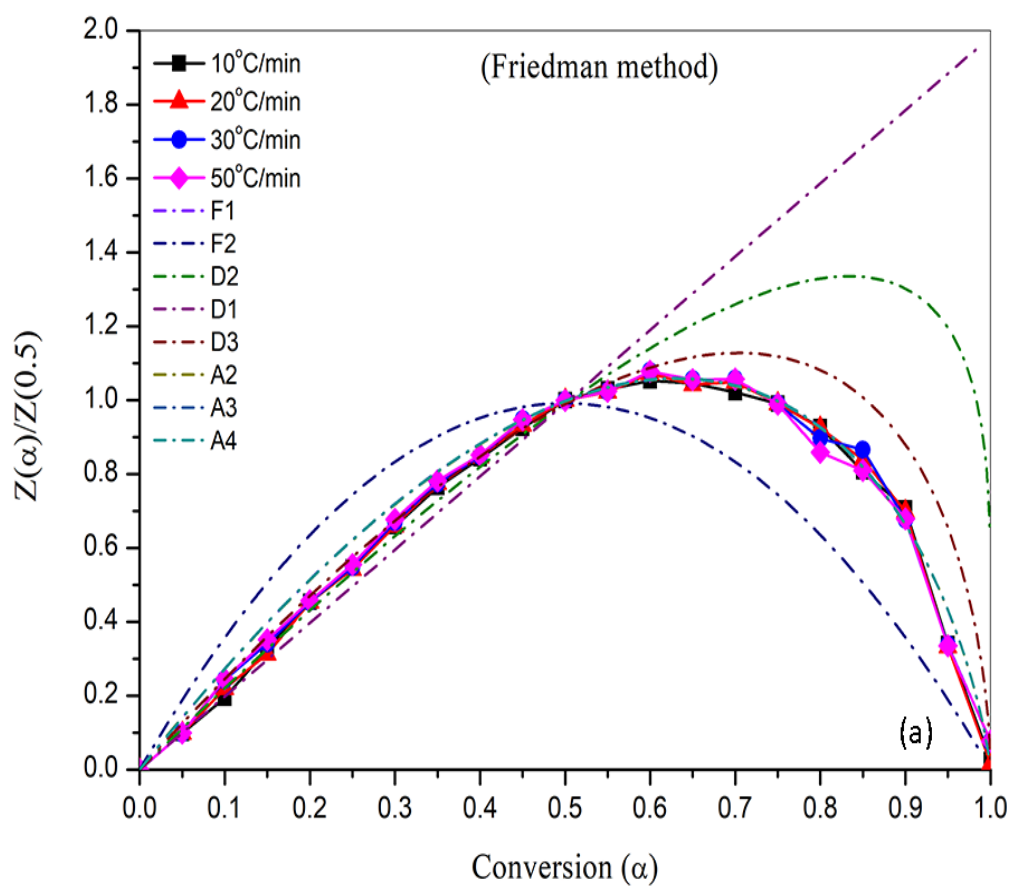


Fig A3. Criado master plot for kerogen degradation using Friedman method.

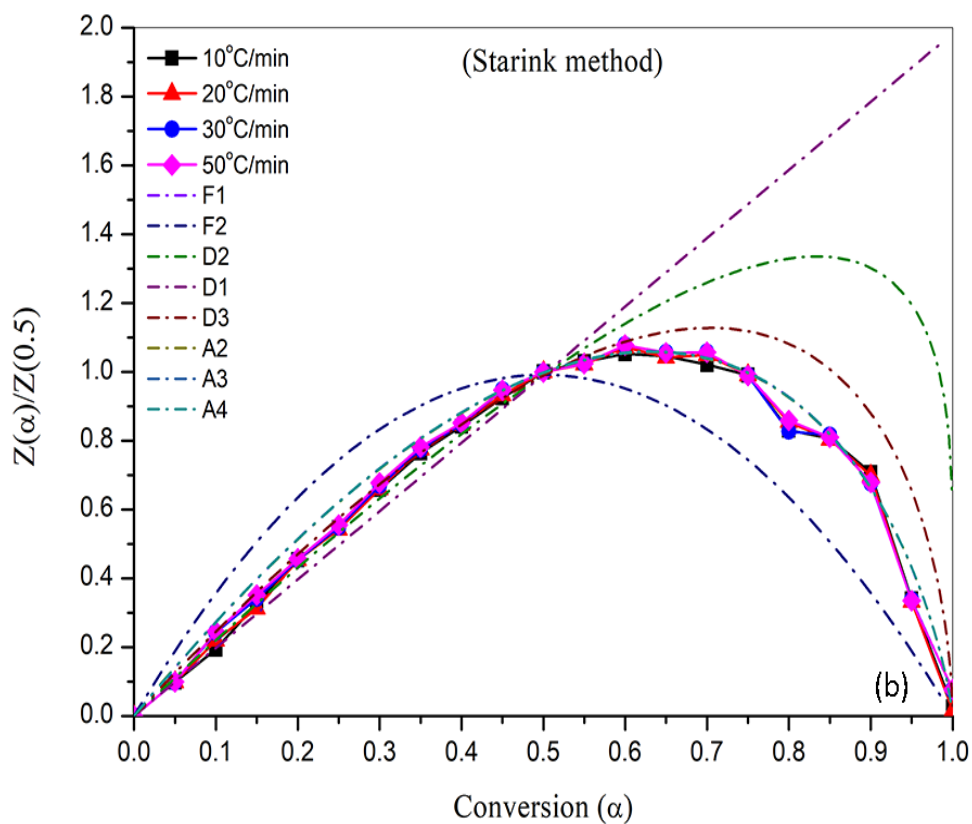


Fig A4. Criado master plot for kerogen degradation using Starink method.

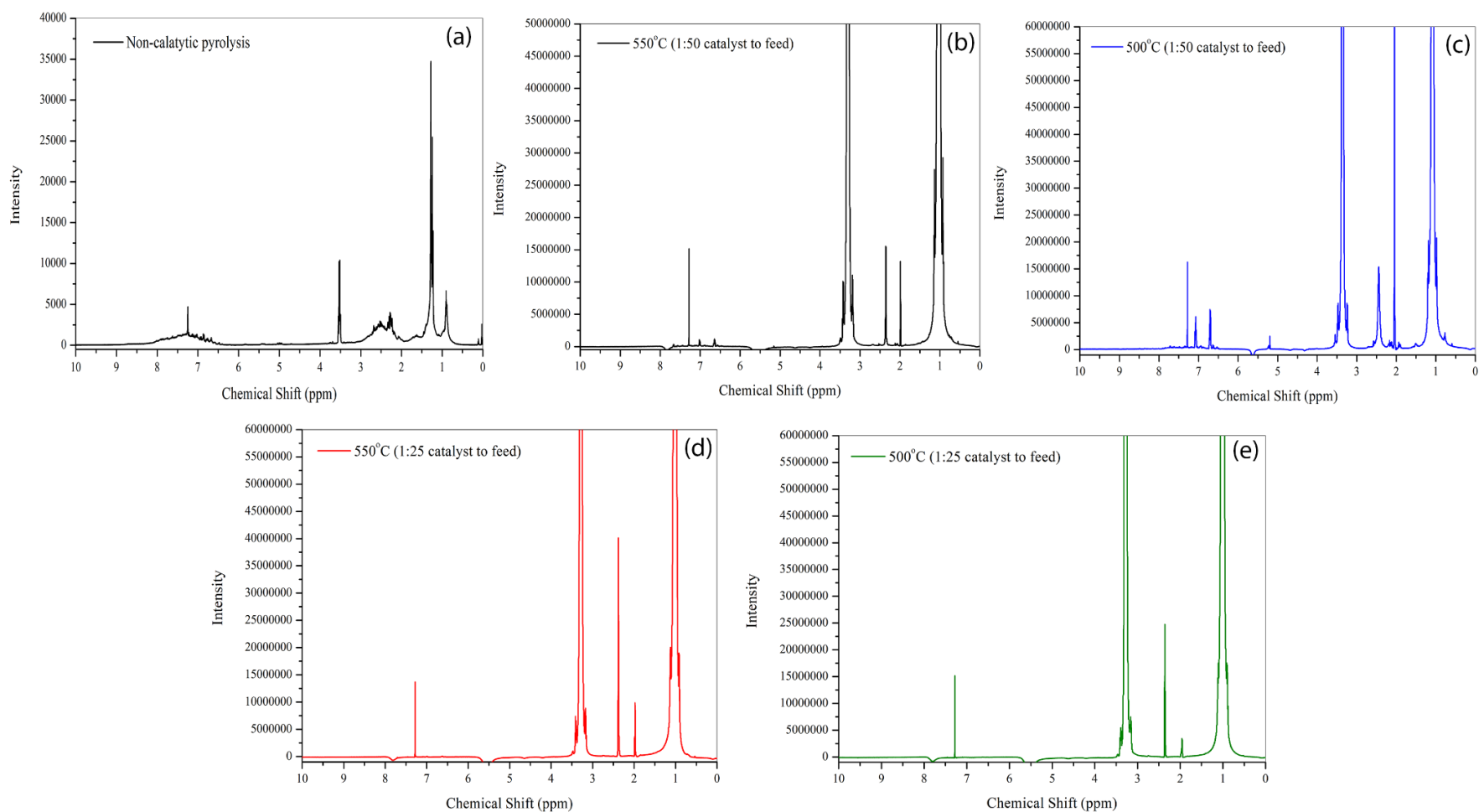


Fig A.5. ^1H NMR spectra of pyrolytic oil obtained at (a) non-catalytic condition at 600°C and heating rate of 10°C [22], and at catalyst to feed ratio of 1:50 and catalyst bed temperature of (b) 550°C (c) 500°C, and at catalyst to feed ratio of 1:25 and catalyst bed temperature of (d) 550°C, and (e) 500°C at pyrolysis condition of 10°C/min and 600°C.