Abstract

Coal and sawdust are viable feedstock substitutes for fuel production. It generates liquid oil, char residue, and fuel gas as the crucial elements of pyrolytic products during the co-pyrolysis process. The blending of biomass with coal helped to decrease the thermal stability of coal. However, the lower thermal stability, lesser viscosity, high oxygen content, high water content and lower calorific value of liquid fuel renders it economically precarious. In addition, fuel gas and char residue also hold as a salient yardstick to this technology since its applications are multifarious. To incessantly mark this challenge, the present study aims to develop a sustainable process that implements functional composite nano-catalysts synthesized by incipient wetness impregnation technique. In the present study, the blended feeds at 10 %, 30 %, 50 %, 70 %, 90 %, 100 % and 200 % were visualized for their degradation potential, and their poitive and negative chemical synergistic effects were estimated from 303-1173 K temperature at various heating rates 10-40 K min^{-1} under nitrogen as purge gas (20 mL min^{-1}) in a thermogravimetric analyzer. The blends with the highest reactivity were studied for their devolatilization kinetics via the Kissinger-Akahira-Sunose method and thermodynamics along with their prediction of theoretical reaction mechanistic pathways. The synthesized catalysts, 10% and 20% NiO and Ni (II) aluminate composite nano-catalysts showed a significant observation in their purity of elements, purity of phases, crystallinity, higher thermal stability, lesser particle sizes, and porosity. The highest degradability and conversion % in the active pyrolytic zone of catalytic pyrolysis of sawdust and catalytic co-pyrolysis of blends ensued the selected (catalyst/sawdust) and (catalyst/blend) ratio for further pyrolytic experiments. The pyrolytic experiments were conducted in a fixed-bed reactor with nitrogen as the purge gas (18 L h^{-1}) at 30 K min^{-1} heating rate from 773–873 K temperature at 1 bar pressure. Due to a larger number of surface-active sites and enhanced oxygen-carrying capacity, the conversion % increased substantially in sawdust pyrolysis with a 20 % Ni loading catalyst. This is mainly accountable to the increased pyrolytic syngas yield with increased H_2 content due to reverse water-gas shift reaction. Aromatic content increased for bio-oil with 20 % Ni loading catalyst due to the catalytic cracking at higher temperatures. The catalyst decreases the oxygen and nitrogen content in bio-oil, thus increasing its fuel quality. Biochar revealed amorphous graphitic multilayer nanosheets with a hexagonal crystal system and a porous carbon structure. However, for thermal pyrolysis of coal, coal char yield % decreased with an increase in temperature from 773–873 K with negligible liquid oil generated as a product. In thermal co-pyrolysis of coal and 100 % sawdust blend, with an increase in temperature from 773–873 K, liquid oil yield increased while biochar yield decreased significantly. However, char residue similarly revealed amorphous graphitic multilayer nanosheets with a hexagonal crystal system. At a coal-sawdust blending of 50 %, 100 % and 200 %, the conversion, wt. % increased from 27.97 % and 37.35 % to a significant rise of 92.8 % respectively. This was due to the synergistic interactions of alkali and alkaline earth metals (AAEM) in the feeds which have an autocatalytic effect on the long-chain aromatic hydrocarbons of coal. With the integration of catalyst to the blends, higher conversion, wt. % was observed significantly with a higher gas yield with a higher metal loading %. Aromatics content increased in the liquid oil for co-pyrolysis of blend with 20 % Ni loaded catalyst, enhancing its fuel quality. This proves that 10 % and 20 % NiO and Ni (II) aluminate composite nano-catalysts are effective functional materials for the catalytic upgradation of pyrolytic products.

Keywords: Coal, Sawdust, Composite catalysts, Co-pyrolysis, Liquid oil, Hydrogen, Char residue