# INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
# SHORT ABSTRACT OF THESIS

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Thesis Title:

**Density Functional Theory Investigations on Upgrading of Phenolic Catalogue of Unprocessed Bio-Oil**

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## SHORT ABSTRACT

In the era of renewable energy resources, biomass is the only renewable energy resource which holds the potential of providing sustainable carbon element useful for transportation vehicles and/or platform chemicals. However, unprocessed bio-oils derived from fast pyrolysis of lignocellulosic biomass exhibit various drawbacks, for instance, low pH, low heating value, low stability, and high viscosity, thus, it cannot be applied directly to transportation vehicles before its upgrading.

In this dissertation, phenolic oxygenated compounds of unprocessed bio-oils are considered as model compounds to investigate their decomposition mechanisms using density functional theory (DFT). Seven phenolic bio-oil model compounds, namely, vanillin, eugenol, ferulic acid, guaiacol, 2-hydroxybenzaldehyde, *p*-isopropenylphenol, and 2-hydroxy-6-methylbenzaldehyde are considered for vapour phase decomposition in the absence of catalyst. Further, guaiacol and 2-hydroxybenzaldehyde compounds are subjected to catalytic hydrodeoxygenation in the presence of Pd(111) catalyst. Moreover, five phenolic bio-oil species, i.e., phenol, 2-hydroxybenzaldehyde, anisole, vanillin, and guaiacol are represented as model compounds to investigate the adsorption phenomena over Pd- and Pt-doped graphene sheets acting as catalysts. Also, a thermochemical analysis is carried out to numerically understand the productions of long range liquid alkanes (C9, C12, and C15) using C6-glucose as representative compound.

During non-catalytic vapour phase decomposition of model compounds, it is found that direct cleavage of functional groups such as methoxy, hydroxyl, allyl, and formyl not kinetically favourable because of corresponding very high bond dissociation energies. However, a single step hydrogenation reaction, at the carbon atom to which a functional group is attached, prior to the scission of functional group delivers a considerably less kinetic barrier. The catalytic hydrodeoxygenation of 2-hydroxybenzaldehyde over Pd(111) catalyst leads to the major production of phenol. The hydrodeoxygenation of guaiacol over Pd(111) catalyst yields catechol as major product. Further decompositions of phenol and catechol from 2-hydroxybenzaldehyde and guaiacol, respectively, are high kinetic demanding reaction steps. On the other hand, phenolic bio-oil model compounds bind strongly to Pd-doped graphene sheets compared to Pt-doped graphene sheets. Finally, the thermochemical analyses of the productions of liquid alkane chains report all participating reactions such as hydrogenation, dehydration and hydrodeoxygenation as favourable except aldol crossed- and self-condensation reactions.