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Catalytic vapor phase upgrading of biomass pyrolysis for the production of phenolic monomers

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Abstract

This study focuses on the thermal conversion of wood sawdust with catalytic vapor phase upgrading to produce high quality biocrude. The activation energy calculated from the thermal decomposition profiles of metal deposited sawdust was found to be maximum (~50 kJ/mol) with Bismuth oxide and minimum (~9 kJ/mol) with Magnesium oxide deposition. Catalytic pyrolysis studies were carried out in a fixed bed reactor with various metal oxides (MgO, ZnO, CuO, NiO, BiO) supported on alumina catalyst at an optimized temperature of 550°C. The effect of nitrogen flow rate, catalyst to biomass loadings on the oil composition were studied and it was found that among the various catalysts studied, magnesium oxide and copper oxide supported catalysts produced high amounts of phenolics (~ 58%) with relatively smaller amounts of acids, ketones and furans.

Introduction

Alternative energy sources will aid in reducing greenhouse gas emissions by substituting fossil fuels. Lignocellulosic feedstocks show greater potential for generating biofuels and diverse chemical building blocks. Pyrolysis-based thermochemical conversion processes of these feedstocks is a promising technology for producing bio-crude, biochar and gases. Biocrude from biomass pyrolysis is unstable due to its high viscosity and contains acidic components with significant water content. It is imperative to catalytically upgrade the biocrude for further processing in any refinery. Alternately, the biomass pyrolysis vapours can be directly upgraded during the process to enhance biocrude quality, which is the scope of this study.

Objectives

This study aims to understand the catalytic activity of non-noble metal oxides such as Magnesium, Zinc, Nickel, Bismuth and Copper oxides supported on alumina for the vapor phase upgrading of sawdust pyrolysis at different conditions.

To improve the biocrude quality with direct vapor phase upgrading during biomass pyrolysis.

To determine the biomass kinetics using Thermogravimetric Analysis (TGA) and to understand the effect of catalyst doping on its thermal decomposition behavior.

Methods

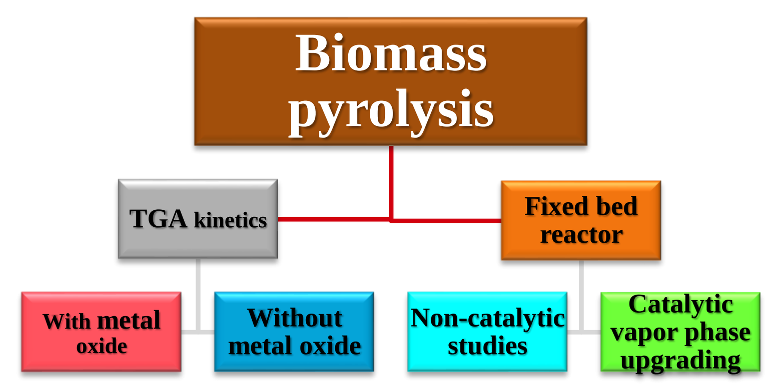

Figure -1: Flow sheet of methodology adapted.

Thermal Decomposition kinetics

TGA of biomass for the active zone of pyrolysis was evaluated using Coats – Redfern method for the estimation of kinetic parameters as this model was found to proven for better estimation of kinetic parameters [1]. The model details are briefly explained below.

$$\frac{\mathrm{Ln}\ g(\alpha)}{T^2} = \ln\left(\frac{AR}{\beta E_a}\right) - \left(\frac{E_a}{RT}\right)$$

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)}$$

$$f(\alpha) = (1-\alpha)^n$$

A plot of $\frac{\ln g(\alpha)}{T^2}$ versus $\left(\frac{1}{T}\right)$ gives a straight line from which the activation energy (E_a) can be estimated. Where, E_a, is the activation energy, A is the frequency factor, n is the order of reaction, T is the temperature, R is the gas constant, β is the heating rate and α is the biomass conversion.

The proximate analysis of the sawdust feed consisted of 11.4% moisture content, ~76 % volatile content, 6% ash and 7% fixed carbon content. These observations are inline with the TGA analysis.

Experimental Set-up

- Custom built fixed bed reactor with an electrically heated furnace
- Reactor: SS316 with ID:4 cm and a heating zone of length 50 cm

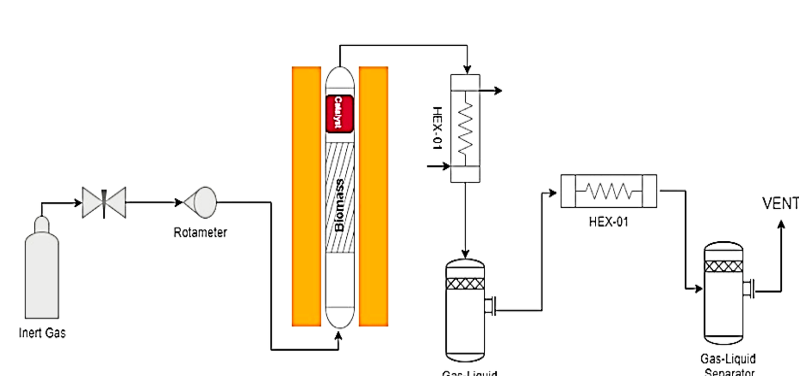

Figure - 2: Schematic of experimental facility.

Results

Catalyst screening for vapor phase upgrading

Under non catalytic conditions, the char yield decreased, bio-crude yield increased with no/minimal changes in the gas yield with increasing temperature. Maximum yield of bio-crude at 550°C (optimum)

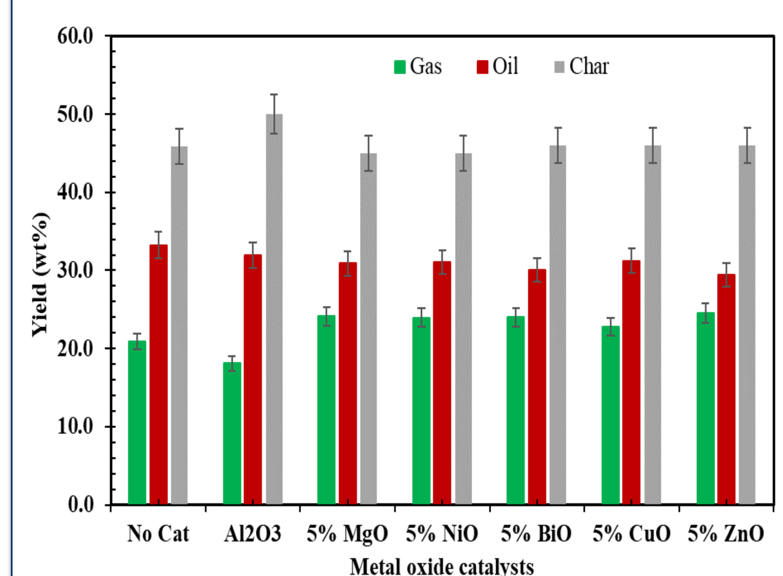

Figure - 3: Effect of different active metal oxides on the pyrolysis product yields.

- Marginally higher gas yields were obtained using MgO and NiO supported catalysts.
- Lower acid content of biocrude with MgO and CuO catalysts while marginally higher hydrocarbon content of bio-crude with BiO catalyst.

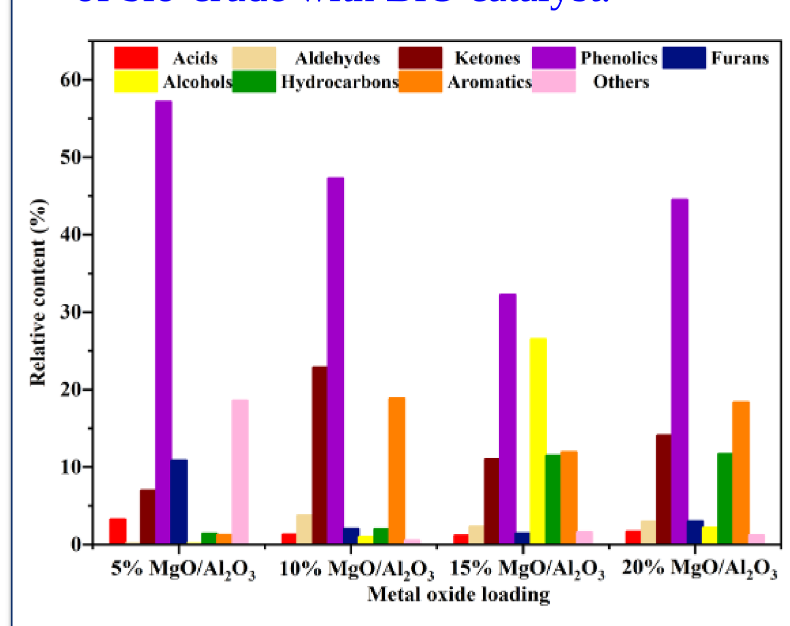

Figure - 4: Effect of different metal oxide loadings on biocrude composition.

- The biocrude product composition varied with increasing MgO loadings.
- The phenolic content decreased while the aromatic content increased with high metal loadings.

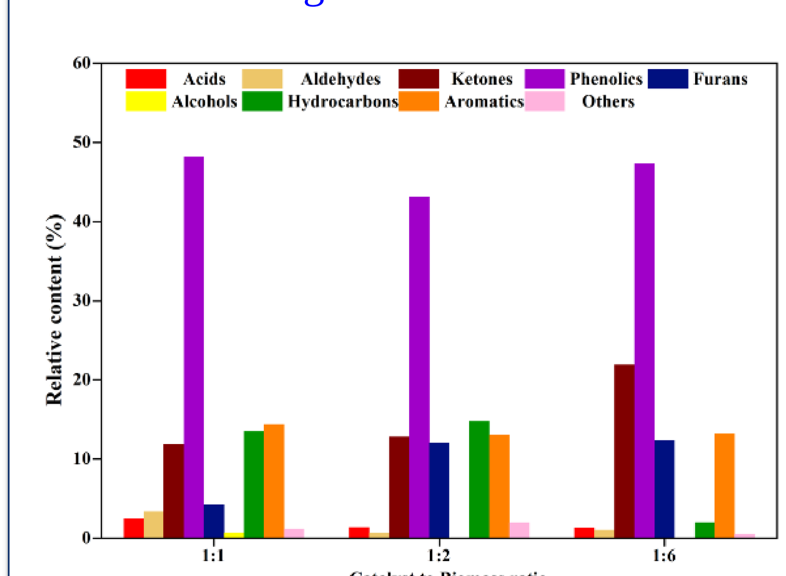

Figure - 5: Effect of different catalyst to biomass ratios on biocrude composition.

- The effect of three different catalyst to biomass ratios was studied.
- A reduction in catalyst quantity resulted in a decrease in the hydrocarbon content of the bio-crude, while there was no significant alteration observed in the proportion of other components.

Discussion

Thermal decomposition studies

The moisture removal up to 150 °C led to ~10% of weight loss. The major weight loss up to ~75% is in the range of 150 – 550 °C. The estimated activation energy of 30, 40 and 50 K/min was found to be 39.5, 31.5, and 26.8 kJ/mol.

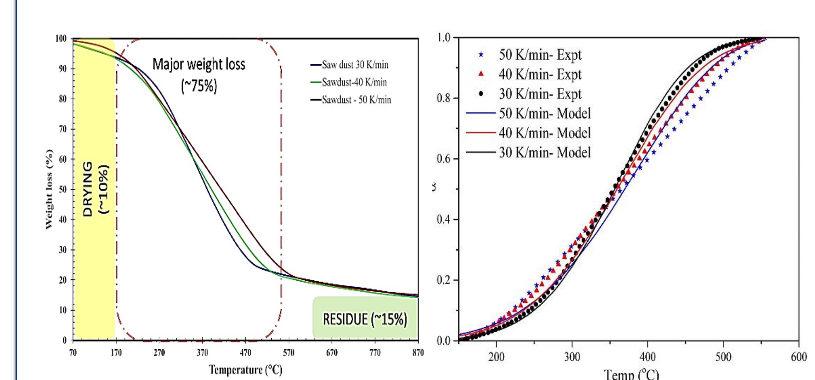

Figure - 6: a) Thermal weight loss profiles b) Experimental vs model prediction using Coats Redfern method.

Conclusions

Thermal decomposition studies

- Activation energy for the sawdust decomposition was in the range of 27 – 40 kJ/mol at different heating rates with the Coats Redfern model that well predicted the experimental data.
- All the metal oxide deposited biomass were found to have a catalytic effect as their decomposition profile was much faster when compared with bare biomass.
- Noticeably, significant differences in the decomposition was observed particularly with MgO.

Catalytic vapor phase upgrading studies

- Only marginal changes in the product yields were noticed in the presence of catalysts.
- The product biocrude composition varied significant with different metal oxide catalysts.
- Studies with higher metal oxide loadings have shown a remarkable decrease in the phenolic content and increase in the aromatic and hydrocarbon content.
- Further studies with high catalyst to biomass ratios have also shown remarkable presence of aromatic and hydrocarbon content.
- In the presence of nitrogen gas, the hydrocarbon content was higher when compared to without nitrogen. Similar findings were noticed with high catalyst to biomass ratios.

Acknowledgements

The authors acknowledge the support provided by the Manipal University Jaipur (MUJ) for carrying out this research.
One of the authors (NC) would like to thank the Commonwealth Scholarship Commission in the UK (CSC) for providing the professional fellowship hosted at University of Strathclyde, Glasgow.

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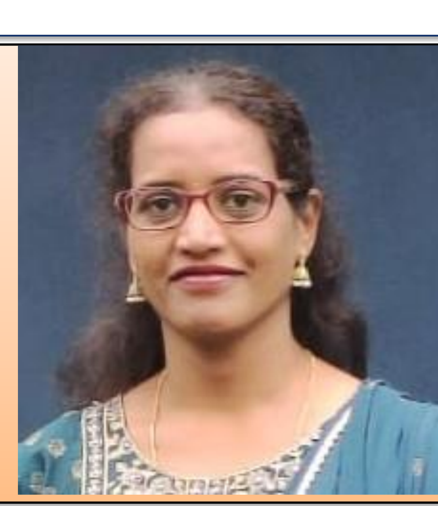

References

1. H.K. Balsora, S. Kartik, T.J. Rainey, A. Abbas, J.B. Joshi, A. Sharma, A.G. Chakinala, Kinetic modelling for thermal decomposition of agricultural residues at different heating rates, Biomass Convers. Biorefinery. (2021).
2. A.K. Varma, L.S. Thakur, R. Shankar, P. Mondal, Pyrolysis of wood sawdust: Effects of process parameters on products yield and characterization of products, Waste Manag. 89 (2019) 224–235.
3. S.D. Stefanidis, S.A. Karakoulia, K.G. Kalogiannis, E.F. Iliopoulou, A. Delimitis, H. Yiannoulakis, T. Zampetakis, A.A. Lappas, K.S. Triantafyllidis, Natural magnesium oxide catalysts: A cost-effective sustainable alternative to acid zeolites for the in situ upgrading of biomass fast pyrolysis oil, App.Cat.B Environ. 196, (2016).

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