Effect of Potassium Carbonate Catalyst on Pyrolysis of Milicia excelsa in a Fixed Bed Reactor

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Abstract - The effect of potassium carbonate catalyst on products distribution from pyrolysis of Milicia excelsa (Iroko) at various temperatures (400, 500 and 600 °C) was investigated. Milicia excelsa sawdust was obtained from a sawmill in Ogbomoso, South-Western Nigeria and was sundried for five days in order to reduce its moisture content. Catalytic pyrolysis of the sawdust was performed with different amounts of catalyst (10, 20, 30 and 40 wt.%). Non-catalytic pyrolysis was also performed for the same temperatures and the products distributions from both batches were compared. Char yield generally increased with increase in catalyst amount for all the temperatures considered. Tar yield did not follow any definite pattern with increasing amount of catalyst as different trends were observed for different temperatures. Gas yield generally decreased with increase in catalyst amount in the feed. Char yields from non-catalytic experiments were higher than those obtained from catalytic runs, with the highest value of 68% at 400 °C. Tar yields from catalytic pyrolysis were higher than those from non-catalytic process at 400 °C (biomass/catalyst ratio of 90/10) and at 500 °C (biomass/catalyst ratios of 70/30 and 60/40), the highest yield being 29.47% at 500 °C and biomass/catalyst ratio of 60/40. Gas yields from catalytic pyrolysis were higher than those from non-catalytic runs except at 500 °C (biomass/catalyst ratio of 60/40), the highest being 51.3% at 600 °C (biomass/catalyst ratio of 90/10). By making use of appropriate biomass/catalyst ratio and temperature, the yield of liquid fuel from catalytic pyrolysis of Milicia excelsa can be increased.

Keywords - Catalyst, potassium carbonate, pyrolysis, biomass, product distribution

1 INTRODUCTION

The continuous growth in economies of the world has placed a high demand on energy supply. Various adventures and interventions have been initiated in order to sustain and further increase the current energy availability. Unfortunately, a high percentage of energy supply still comes from fossil fuels, a scenario that has adversely affected the environment due to the release of greenhouse gases, resulting in ozone layer depletion and the eventual global warming on the one hand and unprecedented depreciation of non-renewable fuel reserves on the other hand. This situation has led to a global campaign for alternative and renewable energy resources, which will be environmentally friendly and having calorific value comparable with conventional fuels. Biomass is one of the promising renewable energy resources. Aside from its adaptability to numerous conversion technologies, biomass is renewable, carbon neutral and almost evenly distributed globally.

In developing countries, biomass accounts for 38 – 43% of primary energy consumption and use of water-based biomass sources and feedstock will continue to be of great importance to research on clean energy generation through biochemical or thermochemical conversion processes (Seo et al, 2010; Demiral and Sensoz, 2008; Balat et al, 2009). Pyrolysis, being a standalone thermochemical process in an inert environment and also a precursor of some other processes (gasification and combustion), has been attracting attention for decades. A lot of studies have been conducted on effect of process parameters, such as pyrolysis temperature, residence time, heating rate, feedstock type, particle size and shape (Demirbas, 2007; Okekunle et al, 2011; Luo et al, 2010; Babu and Chaurasia, 2004; Okekunle et al, 2015; Demirbas, 2004; Wang et al, 2008; Antal and Grenli, 2003; Jahirul et al, 2012) and reactor pressure (Hajaligol et al, 1993; Okekunle and Osowade, 2014; Okekunle et al, 2014; Okekunle and Adeniyane, 2015) on pyrolysis.

Biomass pyrolysis converts 80-95% of feed material to gases and bio-oil (Salleh et al., 2011). Although biomass pyrolysis is a promising source of bio-oil, which is a potential alternative fuel for internal combustion engines, its high viscosity (Thangalazhy-Gopakumar et al, 2012), water content, the presence of highly oxygenated compounds and low H/C ratios (Samolada et al, 2000) have limited its applications. These challenges have necessitated the need for upgrading pyrolysis-derived bio-oil through the use of catalysts. In this regard, a number of researchers have studied the effects of several catalysts on the pyrolysis of different biomass feedstock or biomass-based waste materials (Foster et al., 2012; Zhou et al., 2013; Pütün, 2010; Pütün, Ateş and Pütün, 2008; Zabeti et al., 2012; Yu et al., 2012).

Findings have shown that catalysts do not just influence bio-oil chemical homogenization, stability, water content and oxygen content, they also influence products distribution (Samolada et al, 2000; Pütün, 2010). Virtually in all the above-mentioned studies on catalytic pyrolysis, no woody biomass, typical of West African countries, was considered. This has resulted in lack of data on catalytic pyrolysis of woody biomass in West Africa. This suggests that despite quite a number of potential feedstocks for bio-oil production in sub-Saharan Africa (Odetoye et al, 2019), little work has been done. Therefore, in this study, the effect of potassium carbonate (K2CO3) on Milicia excelsa at different pyrolysis temperatures was investigated. The distribution of solid, liquid and gaseous yields from non-catalytic and catalytic pyrolysis under different conditions are reported. The process conditions for the optimum yield of liquid product from catalytic pyrolysis of Milicia excelsa are also presented.

2 EXPERIMENT

2.1 MATERIALS

Milicia excelsa sawdust was procured from New Sawmill along Ilorin-Ibadan express way, Ogbomoso, South-Western Nigeria. The sawdust was sundried for five days...
in order to reduce its moisture content and the same was stored in a polyethylene bag so as to maintain its moisture content after sun drying. Potassium carbonate (K₂CO₃) was procured from a chemical vendor in Ogbomoso.

2.2 **EXPERIMENTAL SETUP**

The pyrolysis unit comprises of a fixed bed reactor, retort, pipes and hoses, tar traps, heating element, contactor, pyrometer, thermocouple and gas collector unit. The electrically powered fixed bed reactor heated the pre-loaded retort, hence giving off the volatile stream. The product hose channelled the volatile stream into the tar trap collectors which were immersed in an ice-bath. Staged bio-oil trapping was employed to trap the condensable vapour stream which escaped the first bio-oil trap.

Gas collection unit was connected to the tar trap in order to trap the gas stream that escaped the tar traps. Figure 1 shows the exploded view of the pyrolysis unit used for the experiments. The detailed description of this set up has been given elsewhere (Okeakunle et al., 2016).

2.3 **EXPERIMENTAL PROCEDURE**

The experiments were carried out in two batches, one with catalyst and the other without catalyst. The first batch of experiments was done to study the effect of catalyst on products distribution from *Milicia excelsa* pyrolysis at different temperatures while the other was done without the use of catalyst. For the first batch, *Milicia excelsa*/K₂CO₃ weight ratios of 90/10, 80/20, 70/30 and 60/40, thoroughly mixed together, were fed into the crucible, one at a time, and the crucible was covered and fastened with bolts and nuts in preparation for a run.

The furnace was then plugged to the mains, pre-set and heated with the aid of an electric heating element to a temperature 50 °C higher than the desired temperature for pyrolysis in order to compensate for the heat loss during the insertion of the crucible. When the furnace attained the pre-set temperature, it was opened and the crucible was inserted into it. The furnace was covered again and reset to the actual pyrolysis temperature. This procedure was followed for the pyrolysis temperatures of 400, 500 and 600 °C for a residence time of 15 min. After each run, the tar and char yields were determined and expressed in percentages of the weight of the initial sample while gas yield was obtained by mass balance. For the second batch, 100 g of *Milicia excelsa* (without catalyst) was measured and pyrolyzed at 400, 500 and 600 °C for 15 min. The tar, char and gas yields were also quantified following the same procedure as in catalytic pyrolysis.

3 **RESULTS AND DISCUSSION**

3.1 **EFFECT OF CATALYST ON TAR YIELD**

Figure 2 shows char yields for different biomass/catalyst ratios for all the temperatures considered.

From the figure, it is shown that char yield increased with increasing catalyst percentage in the feed with an exception at 500 °C when char yield decreased by 9.01% as catalyst percentage increased from 10 to 20% in the feed. This reduction may be due to some secondary reactions between the char and tar vapour. Afterwards, char yield followed the same trend as in other temperatures. The minimum char yield (33.98%) was obtained at 400 °C and 90/10 ratio while the maximum yield (57.63%) was obtained at 500 °C and 60/40 ratio.

3.2 **EFFECT OF CATALYST ON TAR YIELD**

Figure 3 shows tar yields at different temperatures and biomass/catalyst ratios. It is shown in the figure that tar yield at different temperatures have different trends for the various biomass/catalyst ratios considered. As shown in the figure, at 400 °C, tar yield decreased continuously from 25.92 to 11.49% as the catalyst percentage in the feed increased from 10 to 40%. At this temperature, increasing the percentage of catalyst in the feed resulted in reduction in tar yield. At 500 °C, however, increasing the percentage of catalyst in the feed resulted in a continuous rise in tar yield until it got to the peak (29.47%) for the feed with 40% catalyst. At 600 °C, tar yield increased with increase in the percentage of catalyst in the feed between 10 and 30%, after which a further increase in catalyst percentage in the feed resulted in tar yield reduction.

These results suggest that catalyst addition at 400 °C favoured char and gas formation kinetics at the expense of tar. It is plausible that the lower rate of release of condensable volatile stream from the pyrolyzing solid made more time available for interaction between the tar stream and catalyst, thereby enhancing secondary reactions, resulting in more gas and char yield.
3.3 Effect of Catalyst on Gas Yield

Figure 4 presents gas yields at various biomass/catalyst ratios for different pyrolysis temperatures. As shown in the figure, although gas yields generally were higher at 600 °C than at 400 °C, they followed the same trend, first decreasing with increasing catalyst amount from 10 to 30% in the feed, and second, slightly increasing with a further increase in the catalyst amount. The yield of gas at 500 °C, however, increased with increase in catalyst amount from 10 to 20% after which there was decrease in gas yield with further increase in catalyst amount until it reached the lowest (12.9%) at biomass/catalyst ratio of 60/40. The maximum gas yield of 51.3% was obtained at 600 °C (biomass/catalyst ratio of 90/10).

3.4 Comparison of Catalytic and Non-Catalytic Products Distribution

3.4.1 Char Yield

Figure 5 shows the comparison of char yields from non-catalytic (NC) and catalytic pyrolysis of Milicia excelsa. As shown in the figure, char yields from non-catalytic experiments at all temperatures were higher than those from catalytic pyrolysis, although char yield generally increased with increase in catalyst amount with an exception at 500 °C from 90/10 to 80/20 ratio. This comparison shows that the introduction of potassium carbonate catalyst in Milicia excelsa pyrolysis reduced the yield of char. This suggests the presence of the catalyst enhanced feedstock conversion to liquid and gaseous products.

3.4.2 Tar Yield

Figure 6 shows the comparison of tar yields from non-catalytic and catalytic pyrolysis of the sample. From the figure, tar yield decreased with increasing catalyst amount in the feed at 400 °C while it increased with increasing catalyst amount at 500 and 600 °C (except from 70/30 to 60/40). The figure also shows that tar yields at 400 °C (90/10) and 500 °C (70/30 and 60/40) were higher than all the yields from non-catalytic pyrolysis, the highest yield being 29.47% at 500 °C and 60/40 ratio. The lowest yield was 8.74% at 600 °C (90/10). These results suggest the conditions at which potassium carbonate assisted pyrolysis of Milicia excelsa can be carried out if liquid fuel is prioritized.

3.4.3 Gas Yield

Figure 7 shows the comparison of gas yield from non-catalytic and catalytic pyrolysis of the sample. From the figure, it can be seen that gas yields at all temperatures and biomass/catalyst ratios but one (500 °C and 60/40 ratio) were higher than those from non-catalytic experiments. This suggests that the use of potassium carbonate as catalyst in Milicia excelsa pyrolysis will increase the yield of gas. This increase in gas yield can be linked to the enhancement of feedstock conversion and tar vapour secondary reactions in the presence of the catalyst.
4 Conclusion

Effect of potassium carbonate on the pyrolysis of Milicia excelsa in a fixed bed reactor has been studied. Products distributions from non-catalytic and catalytic experiments were compared. Findings revealed that char yield decreased with increasing temperature for the non-catalytic runs while it generally increased with increasing catalyst amount in the catalytic runs for all the temperatures considered except at 500 °C and from biomass/catalyst ratio of 90/10 to 80/20. Liquid (tar) yields exhibited different trends at different temperatures for catalytic pyrolysis; decreasing continuously with increasing catalyst amount at 400 °C, increasing consistently with the amount of catalyst at 500 °C, and increasing with catalyst amount until it peaked at 70/30 ratio before decreasing with a further increase in catalyst percentage at 600 °C. Gas yields from catalytic pyrolysis were generally higher than those from non-catalytic experiments. For high yields of liquid fuel from catalytic pyrolysis of Milicia excelsa, with potassium carbonate as catalyst, a temperature of 500 °C and feedstock/catalyst ratio within the range of 70/30 - 60/40 should be considered.

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