Effect of Temperature and Catalyst on Biofuel Yields from Pyrolysis of African Copaiba Balsam (*Daniellia Oliveri*) Sawdust

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Abstract - The effect of sodium carbonate (Na_2CO_3) on biofuel yields from pyrolysis of *Daniellia oliveri* sawdust in a fixed bed reactor has been studied. The sawdust was procured from the New Sawmill, along Ilorin-Ibadan expressway, Ogbomoso, South-Western Nigeria. The sample was sundried for three days to reduce its moisture content. Catalytic pyrolysis of the sawdust was performed with different weight percentages of catalyst (10, 20, 30 and 40 wt.%) in the feed. Non-catalytic pyrolysis was also performed for the same temperatures and biofuel yields from both sets of experiments were compared. Char yield increased with an increasing percentage of catalyst and were higher than those from non-catalytic pyrolysis in all but one case, the highest being 49.42% at 500 °C (biomass/catalyst ratio of 60/40) and the lowest, 15.41% at a non-catalytic temperature of 400 °C. Bio-oil yields at 400 and 600 °C followed the same trend up to biomass/catalyst ratio of 70/30 while the yields at 500 °C, though higher than those from non-catalytic experiments in most cases, did not significantly change with an increasing percentage of catalyst. The highest yield of bio-oil (37.64%) was obtained at 600 °C (biomass/catalyst ratio of 90/10) and the lowest (16.41%) at 400 °C (biomass/catalyst ratio of 80/20). Gas yields in most cases decreased with an increasing percentage of catalyst and were all lower than those from non-catalytic experiments, the highest yield (62.77%) obtained at a temperature of 400 °C (non-catalytic) and the lowest (19.73%) at 500 °C (biomass/catalyst ratio of 60/40).
Keywords: Catalytic pyrolysis, biofuel, bio-oil, sodium carbonate, *Daniellia oliveri,* sawdust

1. Introduction

Fossil fuels remain the main sources of energy that are driving the global economy and industrialization. The awareness of the various havocs wrecked on earth by over-dependence on fossils has provoked a global campaign towards reducing their use. Although frantic efforts are being made to find alternatives to fossils, many works still have to be done in getting fuels from renewable sources, which are comparable in combustion characteristics to fossils. For decades, findings have shown that liquid fuel (bio-oil) from biomass pyrolysis can be used as boiler fuel [1] or

29

upgraded to transportation fuels [2-6]. However, high oxygenated compounds in the bio-oil, its high-water content [7] and low H/C ratios [8] have limited its applications. Besides, the acidity, instability and high viscosity [7] associated with pyrolysis-derived bio-oil are also serious concerns. Sequel to this, various chemical processes have been developed for upgrading the bio-oil [9,10]. Amongst these processes, catalytic cracking has been identified as a promising method [8, 11]. In order to understand the effects of catalysts on pyrolysis, several catalysts have been used on different biomass feedstock [12-16]. Aside from upgrading bio-oil, the use of catalysts in pyrolysis has a strong influence on product distribution and can be an interesting approach to product selectivity [17]. Findings from zeolite cracking of pyrolysis oil [18-24] have shown that though zeolite catalysts were effective in oxygen removal, liquid yields were low. Owing to this, less acidic catalysts can be used for bio-oil upgrading while at the same time enhancing liquid yields.

Furthermore, in most previous studies, woody biomass, typical of West African countries, was not used. This has made catalytic pyrolysis data on common West African woody biomass to be very scarce. Therefore, in this study, the effect of sodium carbonate on biofuel yields from pyrolysis of African copaiba balsam (*Daniellia oliveri*) sawdust was studied at different temperatures in a fixed bed reactor.

2. Materials and Methods
2.1 Materials
Daniellia oliveri sawdust was procured from the New Sawmill, along Ilorin-Ibadan expressway, Ogbomoso, South-Western Nigeria. The sawdust procured was the residue from the milling operation of *Daniellia oliveri* trunk at the sawmill. The sample was sundried for three days to reduce its moisture content. After sun drying, it was weighed and bagged in a cellophane bag for it to maintain its

moisture content and it was kept at room temperature until it was used for pyrolysis experiments. Sodium carbonate (Na_2CO_3) was procured from a chemical vendor in Ogbomoso, South-Western Nigeria.

2.2 Experimental setup
Figure 1 shows the exploded view of the pyrolysis unit used for the experiments. A detailed description of this setup has been given elsewhere [25].

2.3 Experimental procedure
Experiments were carried out in two batches, the first with catalyst and the other without catalyst. The first batch of experiments was done to study the effect of catalyst on product distribution from *Daniellia oliveri* pyrolysis at different temperatures while the other was done to study product distribution without catalyst. In the first batch, *Daniellia Oliveri/*Na_2CO_3 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 $^{\circ}$C higher than the desired pyrolysis temperature 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 $^{\circ}$C with a residence time of 15 min. After each run, the bio-oil and char yields were weighed and expressed in percentages of the weight of the initial sample while gas yield was obtained by mass balance. In the second batch, 100 g of *Daniellia oliveri* (without catalyst) was measured and pyrolyzed at 400, 500 and 600 $^{\circ}$C for 15 min. The bio-oil, char and gas yields were also

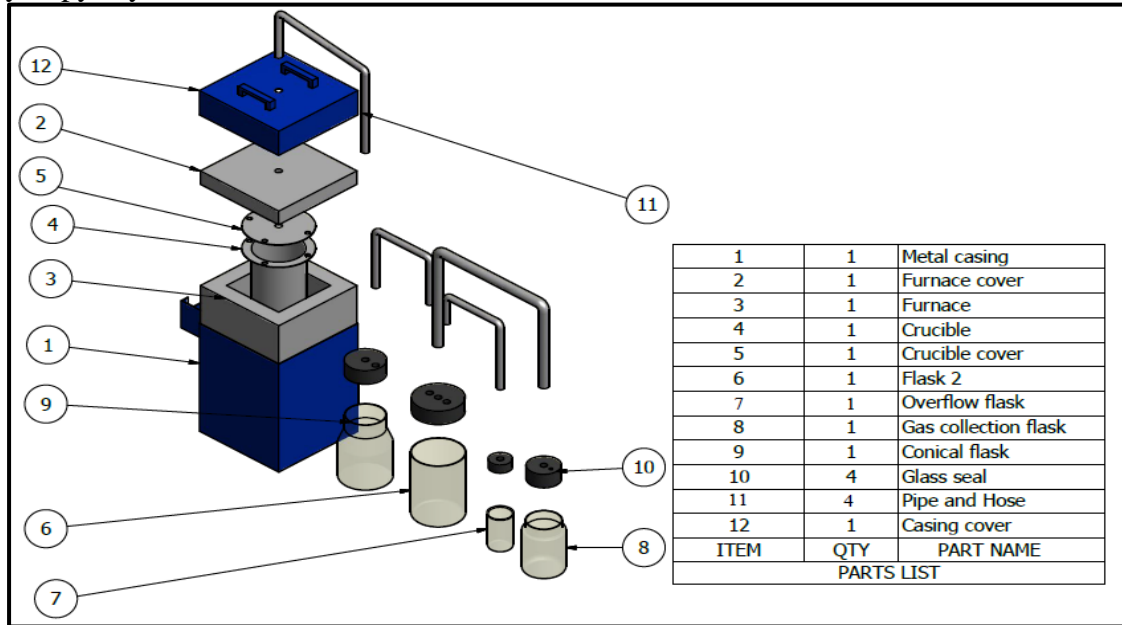quantified following the same procedures as in catalytic pyrolysis.

ITEM	QTY	PART NAME
1	1	Metal casing
2	1	Furnace cover
3	1	Furnace
4	1	Crucible
5	1	Crucible cover
6	1	Flask 2
7	1	Overflow flask
8	1	Gas collection flask
9	1	Conical flask
10	4	Glass seal
11	4	Pipe and Hose
12	1	Casing cover

PARTS LIST

Figure 1: The exploded view of the pyrolysis reactor

3. Results and Discussion
3.1 Effect of catalyst and temperature on char yield

Figure 2 shows char yields at different biomass/catalyst ratios for different pyrolysis temperatures. As shown in Figure 2, the yield of char increased with increasing catalyst percentage for all the temperatures considered. For a biomass/catalyst ratio of 90/10, the highest (32.5%) and lowest (21.69%) yields of char were obtained at 600 and 400 ºC, respectively; for 80/20 ratio, the highest (37.03%) and lowest (33.44%) were at 400 and 600 ºC; for 70/30 ratio, the highest (39.89%) and lowest (35.48%) were at 400 and 500 ºC; and for 60/40 ratio, the highest (49.42%) and lowest (42.40%) were at 500 and 400 ºC. These findings suggest that the effect of temperature on char yield in catalytic pyrolysis is dependent on biomass/catalyst ratio.
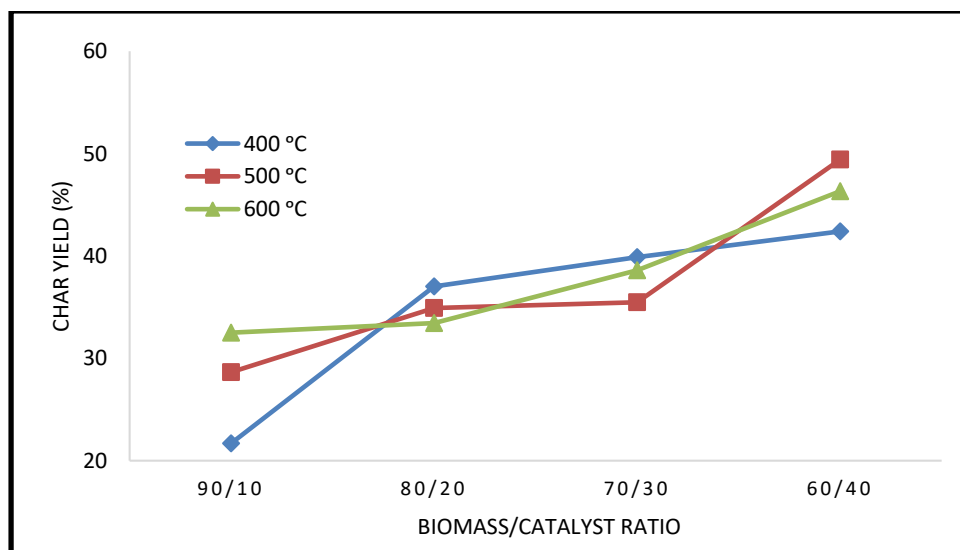
Figure 2: Char yields at different biomass/catalyst ratios and pyrolysis temperatures

3.2 Effect of catalyst and temperature on bio-oil yield

Figure 3 shows bio-oil yields at different biomass/catalyst ratios for different pyrolysis temperatures. As shown in Figure 3, bio-oil yields at 400 and 600 ºC followed the same trend for different biomass/catalyst ratios. An increase from 10 to 20% of catalyst in the feed resulted in bio-oil yield reduction. A further increase in catalyst percentage to 30% in the feed increased bio-oil yield by 13.01% at 400 ºC and by 1.55% at 600 ºC. At a higher percentage of the catalyst (40%) in the feed, bio-oil yield decreased by 11.87% at 400 ºC and by 1.91% at 600 ºC. Unlike at 400 and 600 ºC, different biomass/catalyst ratios at 500 ºC did not cause any significant changes in bio-oil yields, the variation in the yields being in range −0.38 to +3.45%. Figure 3 also shows that the effect of temperature on bio-oil yields at different biomass/catalyst ratios did not follow any consistent trend. However, aside from biomass/catalyst ratio of 90/10, bio-oil yields were maximum at 500 ºC for all other ratios. This finding is very significant for catalytic pyrolysis of *Daniellia oliveri* where the yield of liquid bio-fuel is a priority.
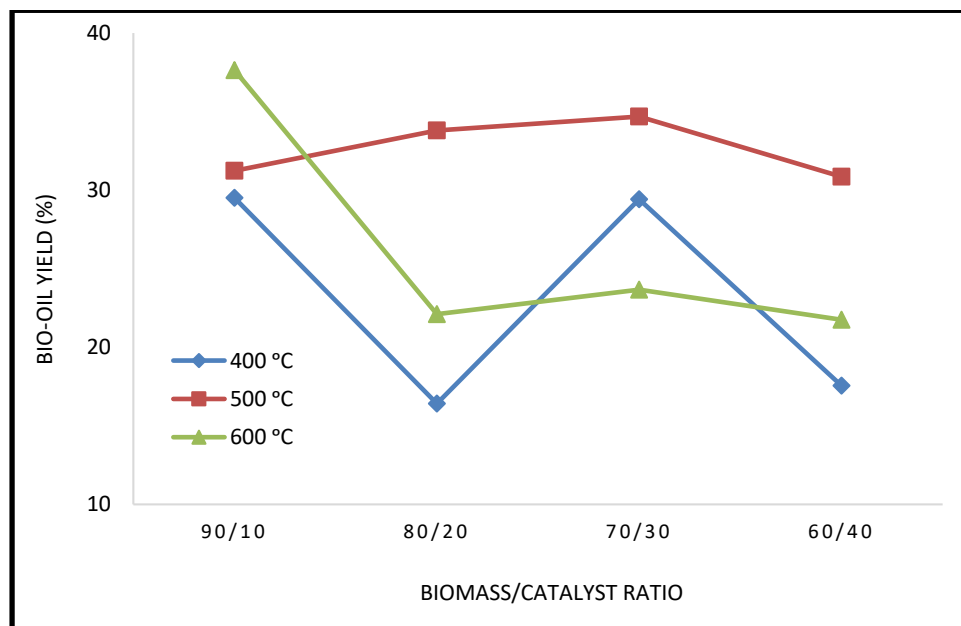

Figure 3: Bio-oil yields at different biomass/catalyst ratios and pyrolysis temperatures

3.3 Effect of catalyst and temperature on gas yield

Figure 4 shows gas yields at different biomass/catalyst ratios for different pyrolysis temperatures. As shown in Figure 4, gas yields at 400 and 500 ºC followed the same trend up to biomass/catalyst ratio of 70/30. An increase in catalyst percentage in the feed from 10 to 20% resulted in a reduction in gas yield by 2.24% at 400 ºC and by 8.85% at 500 ºC. A further increase in catalyst percentage to 30% in the feed further reduced gas yield by 15.87% at 400 ºC and by 1.44% at 500 ºC. However, at a higher percentage (40%) of catalyst in the feed, gas yield increased by 9.36% at 400 ºC while it decreased by 10.11% at 500 ºC. It is necessary to point out, as shown in Figure 4, that gas yield decreased consistently with increase in catalyst percentage at 500 ºC, with the lowest yield (19.73%) in all of the catalytic

experiments obtained at this temperature at biomass/catalyst ratio of 60/40. Unlike the trends observed at 400 and 500 °C, an initial increase in catalyst percentage from 10 to 20%

in the feed increased gas yield by 14.59% at 600 °C. Beyond this catalyst percentage, any increase in catalyst percentage resulted in a continuous decrease in gas yield at 600 °C.
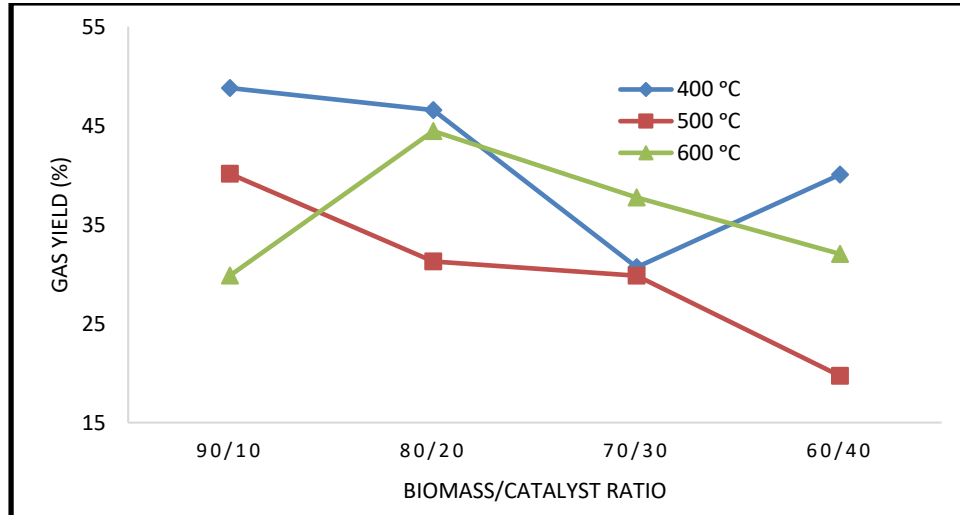

Figure 3: Gas yields at different biomass/catalyst ratios and pyrolysis temperatures

3.4 Comparison of catalytic and non-catalytic product distribution

3.4.1 Char yield

The comparison between char yields from non-catalytic and catalytic pyrolysis of *Daniellia oliveri* is shown in Figure 5. It is shown that char yield increased with the percentage of catalyst at all temperatures in the catalytic experiments. It can also be seen from Figure 5 that char yields from the catalytic runs at all biomass/catalyst ratios at
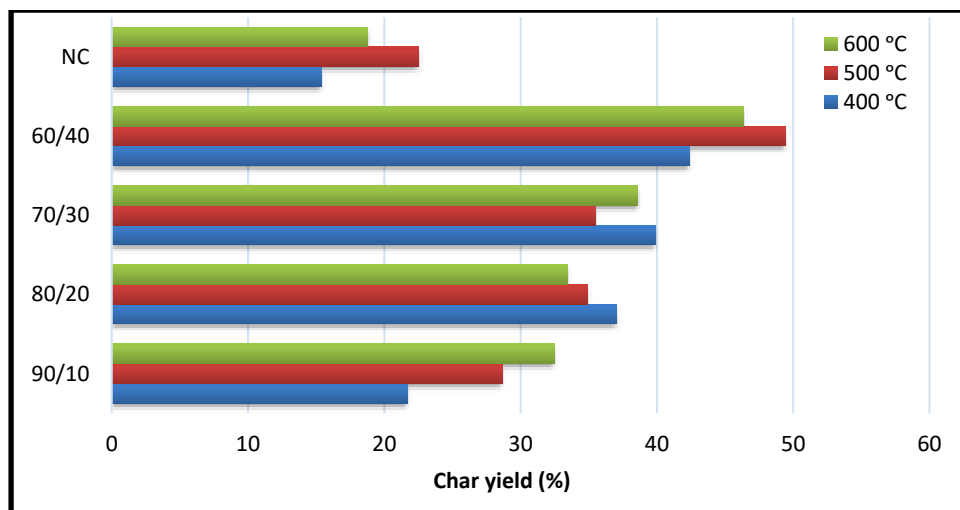

Figure 5: Comparison of char yields from non-catalytic (NC) and catalytic pyrolysis

a particular temperature are higher than the yields from non-catalytic runs at the same temperature. Moreover, it is shown that char

yields from all the cases but one (at 400 °C and biomass/catalyst ratio of 90/10) of catalytic runs were higher than those from non-catalytic

runs. These results show that the use of sodium carbonate as catalyst increased the yield of char from pyrolysis of *Daniellia oliveri*.

3.4.2 Bio-oil yield

Figure 6 shows the comparison between bio-oil yields from non-catalytic and catalytic pyrolysis. It can be seen that in most cases, bio-oil yields from catalytic pyrolysis at 500 °C were higher than all the yields from non-catalytic runs. Figure 6 also shows that the highest yield of bio-oil in all the runs (catalytic and non-catalytic) was obtained at 600 °C and biomass/catalyst ratio of 90/10. These results,

considered together with char yield trends, can inform the choice of the appropriate conditions for maximizing the yield of liquid fuel from catalytic pyrolysis of *Daniellia oliveri*.

3.4.3 Gas yield

Gas yields from non-catalytic and catalytic experiments are compared in Figure 7. It is shown that gas yields from non-catalytic experiments were higher than all the yields from catalytic pyrolysis. These results show that the use of sodium carbonate as catalyst reduced the yield of gas from pyrolysis of *Daniellia oliveri.*
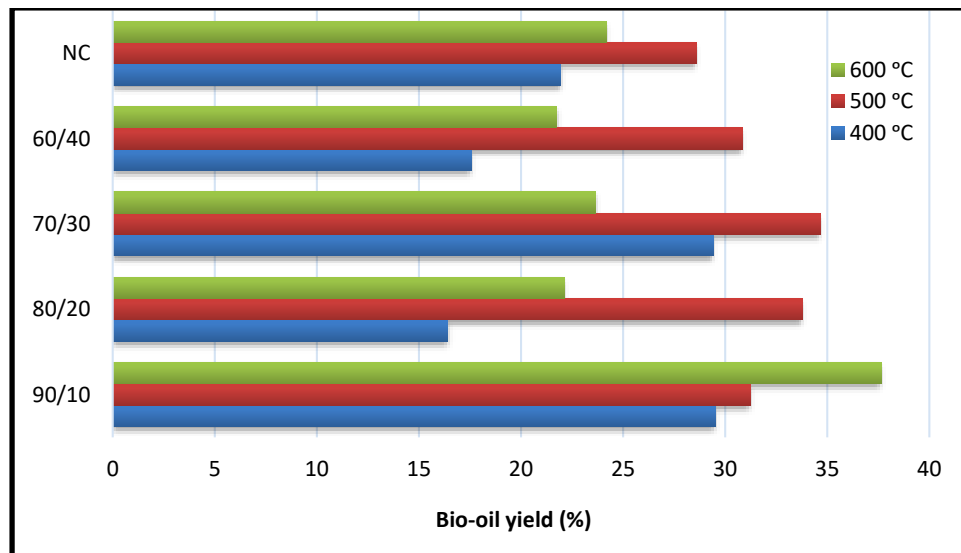

Figure 6: Comparison of bio-oil yields from non-catalytic (NC) and catalytic pyrolysis
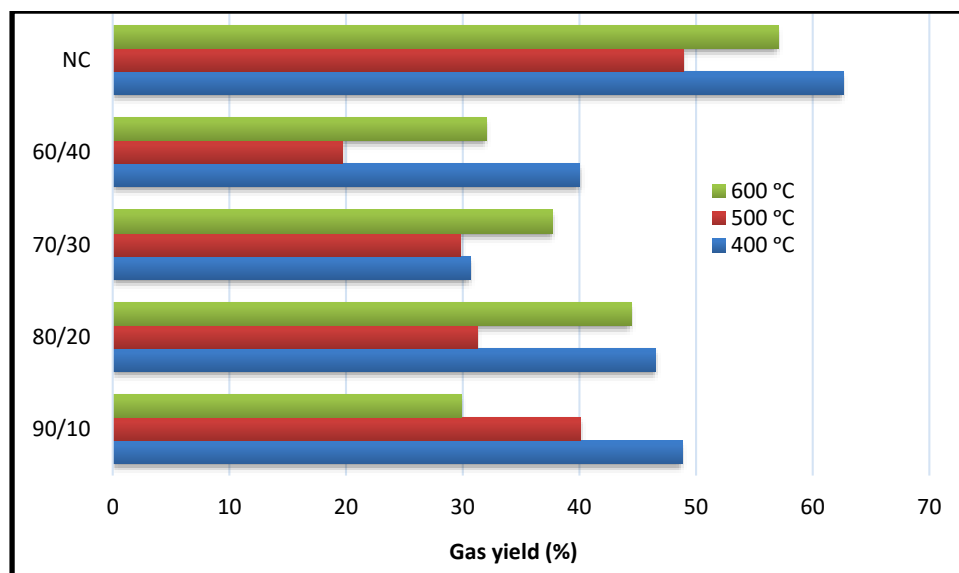
Figure 6: Comparison of gas yields from non-catalytic (NC) and catalytic pyrolysis

4. Conclusions

In this study, the effect of sodium carbonate catalysts on biofuel yields from pyrolysis of *Daniellia Oliveri* sawdust has been studied. Char, bio-oil and gas yields from catalytic pyrolysis were compared with those from non-catalytic experiments. Based on the findings from this work, the following conclusions were drawn:

 i. Char yield increased with an increasing Na_2CO_3 catalyst in the feed for all the pyrolysis temperatures considered.

 ii. Gas yield decreased with an increasing Na_2CO_3 catalyst in the feed for all the pyrolysis temperatures considered.

 iii. Bio-oil yields at 500^oC were not significantly affected by increasing the percentage of Na_2CO_3 catalyst in the feed.

 iv. Bio-oil and char yields from Na_2CO_3 – assisted pyrolysis were generally higher than those from non-catalytic experiments.

 v. The presence of Na_2CO_3 in the feed reduced gas yield for all the temperatures considered.

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