Effect of Varying Physical Parameters on the Products of the Thermochemical Liquefaction of Kraft Lignin using Ni-6458P Catalyst

Soile Olutola O. Bob
Department of Chemistry and Biochemistry, Caleb University, Imota, Lagos, Nigeria

Abstract
Thermo chemical liquefaction of Kraft lignin using Ni-6458P catalyst produced gaseous, aqueous, char and oil products at $350^{O}C$ under 40 atm hydrogen and 40atm carbon monoxide respectively. The effect of temperature , pressure, and feedstock variation on carbon based yield(%yield), carbon based conversion (%conversion), mass of carbon and hydrogen recovered as oil (%CHR), H/C and O/C atomic ratio of oil product and the distribution of gaseous ,aqueous ,char and oil products were studied.ICI lignin was a better feedstock than Kraft lignin in terms of quality , yield and %CHR. CO proved to be a better reductant with the highest products yield. Oils having more desirable quality in terms of H/C and O/C atomic ratios were obtained at zero reaction time at $350^{0}C$.The study also showed that products can also be obtained at lower and more economical conditions than specified in a standard run including, reactions in vacuum and at zero reaction time without a catalyst or reductant at $350^{O}c$.

1. Introduction

The worldwide challenges in energy supplies have prompted quite a number of approaches directed towards an implementation of the use of materials other than petroleum for their energy value. Among these approaches are the renewed interest in the utilization of agricultural and forest products as conventional sources of fuels and chemicals [1,2]. Wood is made up of cellulose, hemicellulose and lignin components [3], with lignin typically 30% by weight. Large amounts of lignin and lignin containing residues are obtained from the pulp and paper industry where lignin-derived compounds can be produced from pulp waste liquor.The model structure of lignin is generally assumed to be a three-dimensional amorphous cross-linked biopolymer which consists of phenyl-propane units, optionally substituted with methoxy and hydroxyl groups. It comprises 15–30% by weight and up to 40% of energy of biomass [4]. In plant cell walls, it is found in the spaces between cellulose and hemicellulose, holding the lignocellulosic matrix together and adding rigidity to plant material [5]. The potential of lignin as a useful feedstock for the production of useful low molecular weight chemicals or fuel additives has been reported [6,7]. Lignin derived from abundant and renewable resources are nontoxic and extremely versatile in performance and qualities that have made them increasingly important in many industrial applications]. Utilisation of lignin is significantly growing due to an increasing interest in renewable raw materials. However, only a part of the lignin is used despite its large potential as a petrochemical substitute for polymers and low molecular weight chemicals. Presently, economic and technological considerations still preclude a large-scale mass production of low molecular weight chemicals from lignin in competition with petrochemicals because of its high oxygen content which translate to a high O/C atomic ratio. Despite the recalcitrant nature of the complex and stable lignin polymer, which makes it difficult to convert it into valuable monomeric chemicals, lignin has been reported to be broken down to monomeric or low molecular weight compounds by a variety of routes, such as thermochemical liquefaction, alkaline oxidation or hydrolysis, alkali fusion, alkaline demethylation , hydrogenolysis and pyrolysis [9]. High pressures and temperatures in addition to the use of catalyst are required for the optimum conversion of lignin to low molecular weight compounds in good yield [10]. The role of catalysts in the conversion of lignin feedstock to various bulk chemicals or fuel components using various catalysts has been reported. [11]. Biofuel produced by liquefaction of lignocellulosic biomass proves to be a promising potential raw material for liquid energy carriers and in particular liquid transportation fuels [12]. Against this background, this study aims to investigate the effects of temperature,pressure,slurry solvent,feedstock,reaction time variation on product distribution and the quality of oil viz: percentage yield (%y), percentage conversion (%x), percentage C+H recovered as oil (%CHR), H/C and O/C atomic ratios.

2. Experimental

The feedstocks used in the study ware (i) a dark brown powdered Kraft lignin processed from straw was obtained from the Department of Biochemistry, University of Manchester, Institute of Science and Technology, Manchester M601QD, UK and (ii)

brown granular lignin,Batch Li/S/S produced by Biological Products Division,ICI PLC,Cleveland,England from straw and wood wastes based on a new recycling process using a high speed catalyst.The Kraft lignin was used mainly in this study with the ICI lignin just providing a basis for comparison. The feedstocks were characterized to ascertain their elemental and moisture composition. The suspension medium, tetralin (3, 4 tetrahydronaphthalene) supplied by Hulls Limited was used as the main organic solvent . The catalyst,Ni6458P, a dry black powderd nickel based catalyst supplied by Harshaw-Chemie BV . The thermochemical liquefaction of Kraft lignin was carried out by charging a previously pressure tested autoclave with the 50g of feedstock, 400g of suspension medium and 1g of catalyst with continual stirring to ensure slurry. The autoclave was sealed off after the charge and clamped in an electric furnace in the reaction cell. The autoclave was evacuated with an in-line cold trap and a vacuum pump at 20mmHg and pressurised to 40atm with hydrogen, carbon monoxide, as the case may be and thereafter the furnace was switched on and allowed to warm up the autoclave and its contents to attain the specific reaction temperature after which the reaction proceeded further for a further reaction time of two hours at the fixed temperature. The normal air breathing apparatus was used to avoid the risk of inhalation where carbon monoxide was used .Temperature-pressure-time were recorded at a regular interval as a means of monitoring the reaction. The furnace was switched off at the end of two hours reaction time and the autoclave with its contents were allowed to cool gradually overnight with continuous agitation and discharged when it had cooled to room temperature. The reactions were carried out at three different fixed reaction temperatures of 300, 350 and 375°C. Pressurization at 20, 40 and 60 atm effected with H_2, CO as reductants respectively and a reaction was carried out in vacuum obtained at 20mmHg. After the reaction, product gas which was a mixture gases and volatile organic compounds generated by the reaction were collected through a gas storage system comprising a vacuum pump, several pre-evacuated glass storage bulbs of known volumes and an in-line nitrogen cold trap for further analysis while the product mixture of solid and liquid products was transferred and were subjected to atmospheric distillation for the separation and collection of aqueous and organic components using a standard laboratory equipment and a heating mantle to avoid the use of naked flame in a fume cupboard until the first sign of the distillate at about 60 °C up to 98°C when the last drop of distillate appeared. The process took about three hours. The atmospheric residue was subjected to vacuum distillation at 1.5mmHg principally for the recovery of slurry solvent- tetralin between 30-50 °C using a vacuum pump, vacuustat and standard laboratory equipment including a heating mantle and an in-line liquid nitrogen cold trap to trap any volatile component which were not completely removed during the initial atmospheric distillation. The process took about three and a half hours .A procedure to reduce the about seven hours for both atmospheric and vacuum distillation processes was later successfully devised by by-passing the atmospheric distillation stage and adapting the vacuum distillation approach at room temperature with constant stirring and with no heat applied at 1.5mmHg. Under these set of conditions all the volatile materials were trapped in the cold trap. This procedure took about one hour followed by applying heat to remove the slurry solvent in the 30-50°C range. The resultant oil fraction was refluxed in acetone, centrifuged at 2000rpm and filtered under water vacuum using a buchner funnel and Whatman no 1 filter paper and washed severally until the filtrate became clear to ensure separation of the acetone insoluble char from the acetone soluble oil. The combined char from the bottom of the centrifuge and the filter paper was placed in a watch glass , dried in an oven at 100°C overnight, cooled in a desiccators and its weight which included the spent or recovered catalyst was determined. The acetone soluble material which is black and viscous, hereafter referred to as the oil was recovered by stripping the acetone on a rotary evaporator underwater vacuum. The high value of carbon and hydrogen coupled with low value oxygen and ash are particularly desirable for good quality oil.

The elemental analysis provided information on %C, %H, %S and %Ash while %O was estimated by difference.

- Carbon based yield   (%(Y) =   x 100…......................... (1)
- Carbon based conversion (%X) = .   X 100.. (2)
- C+H Recovered as oil (%CHR)   =   x 100…..(3)

Product oil parameters namely, percentage carbon based yield (%Y), carbon based conversion (%X), percentage carbon and hydrogen recovered (%CHR), hydrogen carbon (H/C) and oxygen carbon (O/C) atomic ratios were determined from the analysis of the oil obtained. The schematic diagram [24] of the thermo chemical liquefaction of Kraft lignin is shown in figure 1.

3. Results and Discussion

3.1. Analysis of Feedstock
The results obtained from the chemical analysis of the feedstock are reported in tables 1 and 2

Feedstock	[Wt%] Moisture	[Wt%]C	[Wt%]H	[Wt%]N	[Wt%]O	[Wt%] S	[Wt%] Ash	H/C atomic ratio	O/C atomic ratio
Kraft lignin	4.0	58.8	5.7	1.4	28.5	2.4	3.2	1.16	0.36
ICI lignin	6.7	53.6	5.8	1.1	25.5	0.2	14.1	1.29	0.35

Table 1: Characterization of the feedstocks

Feedstock	[Wt%] Na	[Wt%]K	[Wt%] Mg	[Wt%] Ca	[Wt%] Fe
Kraft lignin	1.0	0.1	0.02	0.1	0.1

Table 2: Trace metal analysis of feedstock

Feed	%Y	%X	%CHR	H/C	O/C
Kraft lignin	72.9	72.0	46.9	1.12	0.15
ICI lignin	75.7	85.2	49.4	1.29	0.09

Table 3: Effect of feedstock variation on product parameters at 350^0C, 40 atm.H_2

Table 1 shows the characteristaion of the feedstocks and the main feedstock in this study is Kraft lignin while the ICI lignin was only used for comparative reasons only. It is important to mention that careful selection preparation and type of feedstock is key to having a dependable and reproducible result .Table 2 shows the metal content of Kraft lignin as the major material of interest using micro analytical techniques of Absorption spectrometry and Flame Emission spectroscopy.

Tables 3 shows the effect of feedstock variation at 350^OC on the two feedstocks in an atmosphere of H_2 as reductant . The results showed a higher conversion, yield and CHR with ICI lignin and in terms of product quality the ICI lignin derived oil showed a higher H/C and lower O/C atomic ratios than those from kraft lignin and that the ICI lignin is a better feedstock. The lower O/C atomic ratio could be explained in terms of the much higher aqueous product obtained from the product distribution of ICI lignin reactions. This may not be unconnected with the higher moisture content of the ICI lignin. Production of CO was however higher in the case of kraft lignin than in ICI lignin. The decrease in the H/C atomic ratio in the case of the kraft lignin could be explained in terms of the amount of hydrogen sulphide gas formed, which is higher in the kraft lignin than in ICI lignin. Kraft lignin contains 2.4% sulphur, while the ICI lignin contains 0.2%(Table 2). It is this sulphur that is been reduced to the sulphide.

Feed	[Wt %] Gas	[Wt %] Aqueous	[Wt %] Char	[Wt %] Oil
Kraft lignin	3.0	9.8	26.0	56.8
ICI lignin	4.6	18.6	26.6	57.6

Table 4: Effect of feestock variation on product distribution at 350^0C, 40 atm H_2

Tables 4 shows the effect of feedstock variation on product distribution in an atmosphere of H_2 . The most obvious feature of the distribution is that the gaseous, aqueous and oil fractions were higher for the ICI lignin than the kraft lignin, when H_2 was the reductant. The aqueous and oil fractions were higher for the ICI lignin than the kraft lignin, which explains the higher yield, conversion and CHR when H_2 was the reductant.

Feed	[Wt %] Y	[Wt %] X	[Wt%]CHR	H/C	O/C
Kraft lignin	55.2	53.5	35.2	1.02	0.20

Table 5: Effect of reaction carried out in vacuum on product parameters at 350^0C

Feed	[Wt %] Gas	[Wt%]Aqueous	[Wt %] CHR	[Wt %] Oil
Kraft lignin	5.4	5.0	40.2	44.2

Table 6: Effect reaction carried out in vacuum on product distribution at 350^0C

Tables 5 and 6 show the effect of the reaction under vacuum condition on product parameters and distribution respectively without a catalyst at 350^OC for comparative analysis.

Pressure (atm)	[Wt %] Gas	[Wt%] Aqueous	[Wt %] Char	[Wt %] Oil
20	3.6	18.2	36.2	39.2
40	3.0	9.8	26.0	56.9
60	2.6	18.2	25.6	72.6

Table 7: Effect of H_2 pressure variation on product distribution at 350^0C

Pressure (atm)	[Wt %] Gas	[Wt %] Aqueous	[Wt %] Char	[Wt %] Oil
20	2.2	11.4	25.6	72.6
40	-	5.0	47.8	31.6
60	0.2	10.0	25.8	69.2

Table 8 Effect of CO pressure variation on product distribution at 350^0C

Tables 7 and 8 show the effect of H_2 and CO pressure variation on product distribution using Kraft lignin as the feedstock respectively .With H_2 as the reductant, there was a decrease in the amount of gases ,char, and oil while the amount of aqueous could be said to be fairly constant apart from the dip at 350^OC .Reaction at 20 atm gave the highest amount of gases and char,and lowest amount of oil .On the other hand reaction carried out at 60atm gave the least amount of gases and char,and the highest amount of oil The amount of

aqueous fraction was fairly constant apart from the drop at 350_0C Apart from the least quantity of gasses reaction at 60atm could be described as best in terms of desirable products.

When CO was used the highest amount of gaseous ,aqueous and oil products were produced at 20atm. The highest amount of char and the lowest amount aqueous product at 40atm.The product distribution at 20atm CO therefore appeared to be the best.

The effect of pressure variation using H_2 and CO on product parameters have been reported in the literature[13] regarding yield, conversion, CHR, H/C and O/C atomic ratios and they are in agreement with the findings in this report.

Temperature ^OC	Wt % Gas	Wt % Aqueous	Wt % Char	Wt % Oil
300	2.0	15.4	30.8	73.0
350	3.0	9.8	26.0	56.5
375	5.4	17.4	19.4	71.0

Table 9: Effect of temperature variation on product distribution at 350^0C 40atm H_2

Temperature ^OC	Wt % Gas	Wt % Aqueous	Wt % Char	Wt % Oil
300	1.4	10.2	30.4	76.4
350	-	5.0	47.8	31.6
375	4.6	11.2	23.8	78.8

Table 10: Effect of temperature variation on product distribution at 350^0C 40 atm CO

Tables 9 and 10 show the effect temperature variation on product distribution in H_2 and CO atmosphere using Kraft lignin as feedstock respectively**.** In general, tables 9 and 10, show that higher temperature leads to higher conversions and the amount of gaseous product than at lower temperatures.. In an atmosphere of H_2 higher temperature resulted in a decrease of the residual char and an increase in the amount gaseous product with dip noticed at 350^0C for the aqueous and oil products. The decrease in the H/C and O/C atomic ratios relative to those of the feedstock reported elsewhere [13] could be attributed to the increased production of water as against the little production of CO and CO_2 in the reactions. The amount of aqueous fractions produced are higher than those of the gases and excessive production of water have been known to decrease O/C atomic ratio to the detriment of H/C atomic ratio. .

Time (Hr)	Wt % Y	Wt % X	Wt % CHR	H/C	O/C
0	83.6	75.2	54.2	1.21	0.11
1	76.9	60.6	49.6	1.16	0.15
2	72.9	72.0	46.9	1.12	0.15
3	76.2	65.1	49.2	1.16	0.14

Table 11: Effect of reaction time variation on product parameters at 350^0C 40 atm H_2

Time (Hr)	Wt % Gas	Wt % Aqueous	Wt % Char	% Oil
0	5.0	17.6	25.4	66.8
1	2.8	17.4	36.4	61.4
2	3.0	9.8	26.0	56.8
3	4.2	18.8	30.6	59.8

Table 12: Effect of reaction time variation on product distribution at 350^0C 40atm H_2

Tables 11 and12 show the effect of reaction time variation in an atmosphere of H_2 on product parameters and distribution using Kraft ligin as a feedstock respectively.The duration of the reaction time did not have a very significant effect on the product parameters and in fact did not follow particular linear trends. The results obtained however at zero reaction time could be favourably compared with the result of reactions held for 3 hours. So in terms of capital cost, the reactions are better carried out at zero reaction time since comparable results were obtained at longer reaction periods and also the best oils in terms of H/C and O/C atomic ratios, yield, conversion and CHR were obtained at zero reaction time. On product distribution, the gaseous product was found to increase with time except for the slight drop at 2 hours reaction time. The aqueous product remains constant except for the drop at 2 hours reaction time. The lowest amount of char and the highest amount of gaseous, aqueous and oil product, were obtained at 3 hours reaction time.Previous studies are available that supported the findings in this study[14] but not on direct liquefaction of straw derived Kraft lignin and process variables used in this study[13].However several have been reported with different starting materials[15]

4. Conclusion

Thermochemical liquefaction of Kraft lignin using Ni-6458P catalyst at elevated temperatures ,pressures and varying atmospheric conditions produced products of varying quality and quantity. The study concluded that thermochemical liquefaction of Kraft lignin has a great potential for the production of materials capable of been used as transportation fuels after further treatment to reduce the undesirable oxygen content and also as a veritable source of low molecular weight chemicals with due to the presence of phenyl-propane repeating units found in lignin structure'

It could be concluded from the results of process variables that the liquefaction process could be carried out without a catalyst or a reductant gas as exemplified by the reaction carried out in vacuum without the use of a catalyst at 3500C. The result obtained could averagely be compared with reactions carried out at the same temperature in the presence of catalysts and reductants.Conversion and yield generally increased with rise in temperature.Two series of reactions were carried out at nominalreaction times varying fro zero to three hours and it was found that satisfactory results were obtained at shorter reaction times,Probably the most desirable overall reaction in converting the lignin to oil would be the splitting out of oxygen to form molecules with high H/C and lower O/C atomic ratios.

With further process optimisation and treatment of liquefaction products through deoxydenation and other advance processes we would see a reduction in envisaged capital cost and acceptable quality.
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6. References

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