Effect of Varying Physical Parameters on Thermochemical Liquefaction Products of Kraft Lignin using 3%Ru/Al$_y$(SiO$_4$)$_x$ Catalyst

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ABSTRACT: Thermochemical liquefaction of Kraft lignin using Ru/Aly(SiO4)x catalyst produced gaseous, aqueous,char and oil at 350OC under 40atm hydrogen and 40atm carbon monoxide, . The effect of temperature , pressure ,slurry solvent, reaction time and feedstock variation on carbon based yield(%Y), carbon based conversion (%X), mass of carbon and hydrogen recovered as oil (%CHR), H/C and O/C atomic ratio of oil parameter and product distribution were studied.ICI lignin was a better feedstock than Kraft lignin in terms of quality and yield.Water /tetralin slurry system gave the highest yield and %CHR .Hydrogen proved to be a better reductant with the highest products yield.The best oils at 350OC in terms of H/C andO/C atomic ratios were obtained at zero reaction time.The study also showed that the capital cost liquefaction of Kraft lignin can be reduced under vacuum at zero reaction time without a catalyst or reductant in a water slurry at 350Oc or below.

Keywords: Kraft lignin, Thermochemical, Liquefaction, Reductants, Reaction time,Process variables,Product distribution

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1. Introduction

The search for alternative energy supplies has renewed interest in the utilization of agricultural and forest products as conventional sources of fuels and chemicals[1,2,3]. Wood is made up of cellulose, hemicellulose and lignin components [4], 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% by energy of biomass [5,6,7]. 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 [8]. The potential of lignin as a useful feedstock for the production of useful chemicals or fuel additives has been reported [9, 10, 11, 12, 13, 14, 15]. 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 [16]. 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 [17, 18]. 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 [19, 20]. The role of catalysts in the conversion of lignin feedstock to various bulk chemicals or fuel components using various catalysts has been reported. [21, 22]. 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 [23]. 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 and compared with tetralin/water slurry(375g/25g). The catalyst,3% $Ru/Al_y(SiO_4)_x$ was ruthenium supported, greyish black spherical pellets obtained from Johnson Matthey Research centre, UK. 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, nitrogen 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, vacuum stat 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 under water vacuum. 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) $= \dfrac{mass\ of\ C\ in\ feed - mass\ of\ C\ in\ char}{mass\ of\ C\ in\ feed}$ x 10…............................ (1)

Carbon based conversion (%X) $= \dfrac{mass\ of\ C\ in\ oil}{mass\ of\ C\ in\ feed}$ x 100 .... (2)

CHR   (%CHR) $= \dfrac{mass\ of\ C\ and\ H\ in\ oil}{mass\ of\ feed}$ x 100…..(3)

Product oil parameters namely, percentage carbon based yield, carbon based conversion, 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 thermochemical liquefaction of Kraft lignin is shown in figure   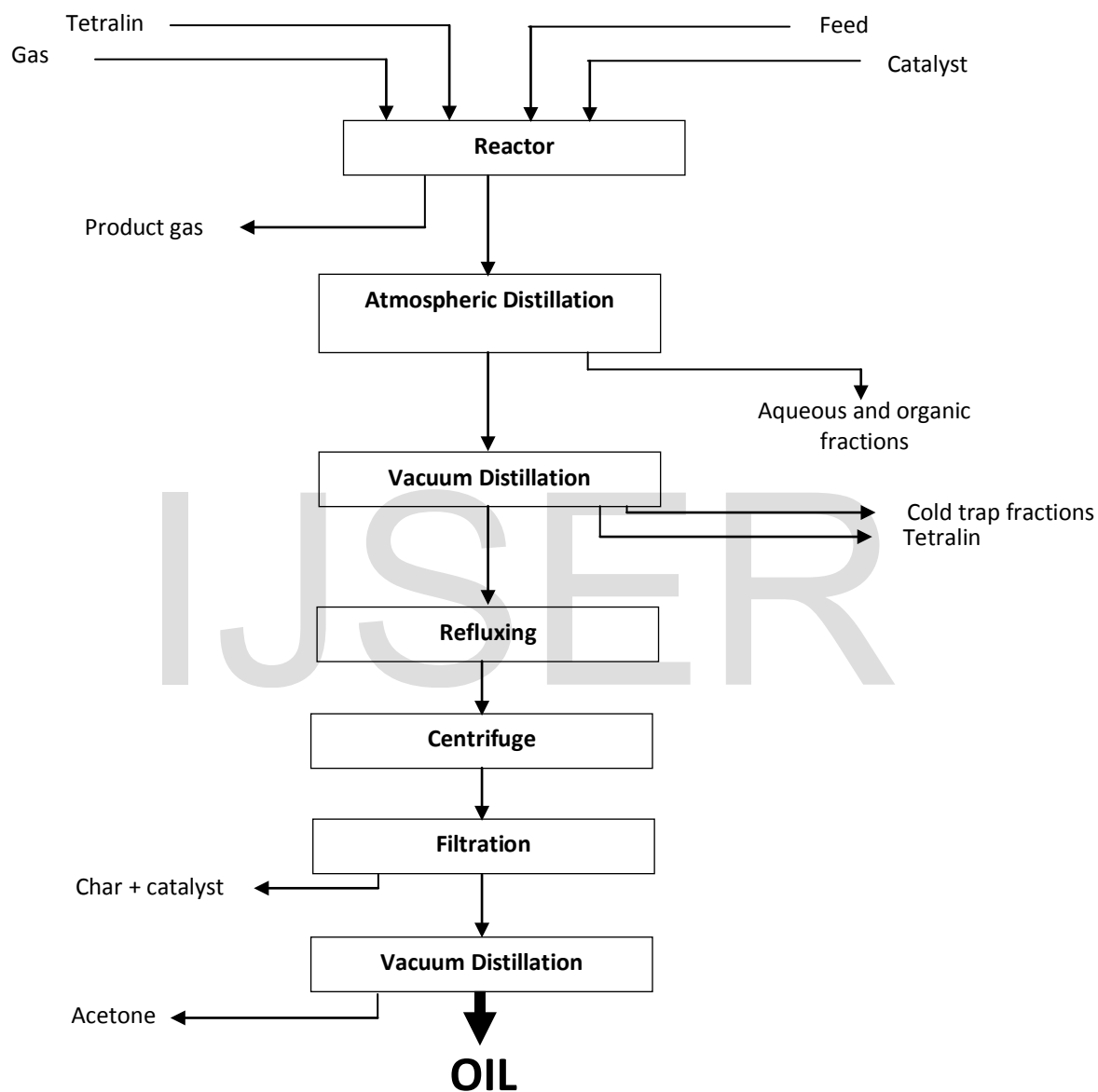   1.

Figure 1: Schematic Diagram of the Liquefaction of Kraft-Lignin [24]

3. Results and Discussion

Unless otherwise stated a stsandard run consists of (i) 50g feedstock , (ii) 1g catalyst , (iii) 400g solvent , (iv) 40atm reductant , (v) 350^{0}C reaction temperature ,(vi) 2 hours reaction time.

3.1 Analysis of feedstock

The results obtained from the chemical analysis of the feedstocks are reported in table 1 while the metallic content was determined only for Kraft lignin as the main feedstock in this study.

Table 1: Characterization of the feedstocks

Feedstock	Wt% Moisture	W% 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	6.7	25.2	0.2	1.29	0.35

Table 2: Trace metal analysis of feedstock

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

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

Feed	%Y	%X	%CHR	H/C	O/C
Kraft lignin	57.3	56.3	36.8	1.08	0.15
ICI lignin	75.5	68.1	49.1	1.23	0.10

Table 4:Effect of feedstock variation on product parameters at 350^0C,40 atm.CO

Feed	%Y	%X	%CHR	H/C	O/C
Kraft iignin	64.6	57.2	41.3	106	0.13
ICI lignin	72.6	73.6	47.4	1.32	0.12

Table 3 and 4 show the effect of feedstock variation on product parameters and distribution at 350^oC under the influence of H_2 and CO respectively. 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 fixed up. The lower O/C atomic ratio could be explained in terms of the much higher aqueous product obtained from the product distribution of kraft lignin pre-actions. This may not be unconnected with the higher moisture content of the ICI lignin. The 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 1). It is this sulphur that is been reduced to the sulphide

Table 5:Effect of feedstock variation on product distribution at 350^0C, 40 atm H_2

Feed	Wt %	Wt % Aqueous	Wt % Char	Wt % Oil
Kraft	3.2	11.9	37.8	44.2
1cl	5.8	16.0	38.8	57.4

Table 6:Effect of feedstock variation on product distribution at 350^OC, 40 atm CO

Feed	Wt %	Wt % Aqueous	Wt % Char	Wt % Oil
Kraft lignin	-	8.4	35.4	48.8
ICI lignin	-	10.0	35.4	57.0

Tables 5 and 6 show the effect of fixed stock variation on product distribution and 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 two feedstocks did not produce any gaseous product when CO was used. 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.

Table 7:Effect of slurry solvent variation product parameters at 350^OC, 40 atmCO

Solvent	Wt % Y	Wt % X	Wt %CHR	H/C	O/C
Tetralin	64.6	57.2	41.3	1.06	0.13
Water/Tetralin	83.4	60.9	54.0	1.06	0.14
Water	68.0	84.9	43.6	1.09	0.14

Table 8:Effect of slurry solvent variation on product parameters at 350^0C, 40 atmCO

Feed	Solvent	Wt% Gas	Wt% Aqueous	Wt % Char	Wt% Oil
Kraft lignin	Tetralin (400g)	-	8.4	35.4	48.8
Kraft lignin	Water /Tetralin (375g/25g)	2.0	4.4	32.6	63.0
Kraft lignin	Water 400g	20.0	-	11.4	52.4

The water/tetralin system (Table 7) gave the highest amount of yield and CHR while the water system alone gave higher amount of yield conversion CHR, H/C, and O/C atomic ratios than the reaction using tetralin alone as the slurry solvent. This makes water a better solvent than tetralin. The water gas shift reaction is probably more effective in the donation of H_2 to the substrate than the tetralin and hence the slightly higher H/C atomic ratio found in the water

reaction. In terms of product quality the O/C atomic ratios were fairly constant. Also the amount of carbon dioxide obtained in the water reaction is higher for the water reaction and only found in trace amount in the tetralin reaction. On product distribution (table 8) no net gaseous output was obtained in the tetralin reaction and only with a small amount of gaseous product when water was included in the slurry while the water reaction produced a greater amount of gases. The amount of aqueous fraction in the tetralin reaction almost doubled the amount produced in the water/tetralin system. There is a likelihood of consumption in the water system alone resulting in the absence of this fraction. The water reaction however produced higher amount of oil and lower amount of char than the tetralin reaction

Table 9: Effect of vacuum condition on product parameters at 350^0C.

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

Table 10:Effect of H2 pressure variation on product distribution at 350^0C

Feed	Wt % Gas	Wt % Aqueous	Wt % Char	Wt % Oil
Kraft lignin	5.4	5.0	40.2	44.2

Tables 9 and 10 show the effect of the reaction under vacuum condition without a catalyst at 350^OC for comparitve analysis

Table 11 Effect of C/O pressure variation on product distribution at 350^0C:

Pressure (atm)	Wt % Gas	Wt % Aqueous	Wt % Char	Wt % Oil
20	3.8	17.0	30.6	60.6
40	3.2	11.4	37.8	44.2
60	11.0	17.8	34.6	63.8

Table 12 Effect of temperature variation on product distribution at 350^0C 40 atm H2

Pressure (atm)	Wt % Gas	Wt % Aqueous	Wt % Char	Wt % Oil
20	12.8	19.2	42.6	48.8
40	-	8.4	35.4	48.8

| 60 | - | 14.0 | 37.6 | 56.4 |

Tables 11 and 12 show the effect of reductant pressure variation on product distribution with hydrogen, no particular trend was followed. However the highest amount of product was produced at 40atm hydrogen, except for the much higher gaseous output at 60atm. In the case CO, the only gaseous output was at 20atm. CO and highest amount of aqueous product were also produced at this initial pressure. The amount of oil produced was the same at 20 and 40atm but highest at 60atm. The highest amount of char was produced at 20atm and the lowest amount ay 40atm. Product distribution at 60atm appears to be the best from the stand point of liquefaction.

Table 13: Effect of temperature variation on product distribution at 350^0C 40atm CO

Temperature ^0C	Wt % Gas	Wt % Aqueous	Wt % Char	Wt % Oil
300	2.4	12.6	43.2	51.4
350	3.2	11.4	37.8	44.2
375	4.0	9.0	31.8	45.0

Table 14: Effect of reaction time variation on product distribution at 350^0C 40 atm H2

Temperature ^0C	Wt % Gas	Wt % Aqueous	Wt % Char	Wt % Oil
300	-	7.6	37.8	60.2
350	-	8.4	35.4	48.8
37	-	13.2	25.8	60.8

In general, tables 13 and 14, show that higher temperature leads to higher conversions and the amount of gaseous product than at lower temperatures. As pointed out earlier, some reactions carried out in the presence of CO did not show any net gaseous output (Table 5). Higher temperature also resulted in the reduction of the residual char and an increase in the amount gaseous and liquid products. The decrease in the H/C and O/C atomic ratios relative to those of the feestock 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. Water removal from the reactions has not been an efficient way of reducing oxygen in this study, though the objective of low O/C atomic ratios has been achieved but increasing the H/C atomic ratio relative to the starting material did not materialise.

Previous researches supported the findings in this study[24,25,26,27,28,29.30].However a lot of reviews and reports were not exactly the same materials and process variables in this study.

Table 15: Effect of reaction time variation on product distribution at 350⁰C 40 atm CO

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 16: Effect of reaction time variation on product distribution at 350⁰C 40atm H$_2$

Time (Hr)	Wt % Y	Wt % X	Wt % CHR	H/C
0	2.6	15.8	36.0	60.0
1	3.6	15.8	34.8	74.6
2	32	11.4	37.8	44.2
3	4.0	16.2	32.6	69.0

Tables 15 and 16 showed that 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.

4. Conclusion

Thermochemical liquefaction of Kraft lignin using 3%Ru/Al$_y$(SiO$_4$)$_x$ catalyst at varying temperature ,pressure ,reaction time, slurry solent and atmospheric conditions including under 20mmHg vacuum produced products of varying quality and quantity capable of being used as transportation fuels and a source of low molecular weight

chemicals after further treatment. The study concluded that capital cost in a venture such as this could be significantly be reducedas evidenced by all the possibilities noted in this study viz: the use lower temperature ,pressure ,cheaper water as any temperature above 350^0C will be close to its critical temperature and will require use of higher pressure to maintain water in liquid phase and with the separation step sometimes encumbered by oil-water emulsion.Also beneficial are the excusion of catalysts , use of vacuum in place of the more expensive H_2/CO and use of zero reaction time.However a lot still needs to be done in the area of product and process optimization.

Acknowledgement

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