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## Thermochemical Liquefaction of Kraft Lignin as A Waste Management Process

Bob Soile\*, Moses Akiibinu, Felix Oyeyiola

Department of Chemistry and Biochemistry, Caleb University, Imota, Lagos, Nigeria.

[bob.soile@yahoo.com](mailto:bob.soile@yahoo.com),

### Abstract

Waste management is the collection, transportation, processing or disposal, monitoring, and managing of waste materials. It tries to reduce the harmful environmental impact of each through different methods, which include but not limited to landfill, incineration, recycling, biological processing, and reduction methods. Generation, utilization, and disposal of waste is increasingly becoming a significant problem in many cities of the world, with an exploding world population estimated to have a global doubling time now less than twenty years. This research focuses on energy recovery as a viable method of disposal of non-hazardous biomass components of municipal solid waste with a prototype waste kraft lignin material using the thermochemical liquefaction process. The process used high pressure, high temperature in the presence of kraft lignin, slurry solvent, and a suitable catalyst to produce a mixture of gases, liquid, and solid capable of been used as fuels and chemicals and providing an alternative to the other methods. This value-adding process serves a dual purpose of providing a source of energy and providing an alternative waste management method.

**Keywords:** Biomass, Lignin, Waste, liquefaction, Oil.

### Introduction

The future stability and welfare of the world are closely linked to the number of its people. Until recently the knowledge of the total world population was rested on very unsecure foundation. However it is possible to estimate the population of the world and conjecture its future. It is obvious that the world's population is probably more than 4.5 billion with a global doubling time now less than 30 years. Population growth rate is accelerating and today it is estimated to be about 2% annually.

The process of urbanization with increasing population will create additional strains on the world energy supplies and increase the problems of waste disposal.

With expected increases in economic development and personal living standards, the increasing bulk of solid waste will undoubtedly have reverberant impacts on the world environment and its people.

The rate of solid waste production is beginning to outstrip the growth in population and this will continue to rise in the future especially in the wake of an increasing degree of industrialization, the lack of land disposal sites and the lack of effective waste disposal technology leading to increasing cost of waste management as reported at a solid waste conversion conference[1].

Generation, utilization and disposal of waste is becoming increasingly a major problem in many of our cities . Lagos, Nigeria ,for example treats 5000T of waste at it

s Olushosun site and 1000T Simpson site respectively daily .With an estimated population of 20million residents generating an average 0.5kg waste per resident per day will translate to 10-12 MT of waste daily as reported by the Punch newspaper [2].



Waste management is capital intensive and involves labour for collection and sorting, packers, trucks including ecological costs of dealing with noise, dust, offensive odour, vermins, CO<sub>2</sub> and CH<sub>4</sub> gas emissions, leaching of soluble components of waste streams into ground water as reported by the Punch newspaper, Soile, Odesanya et al [2,4,5,6]. The most commonly used form of disposal are the landfills because they are relatively cheap and cost effective and has the advantage of providing land fill gas which can be generated and harnessed depending on the quantity of deposit for energy generation purposes. Lagos with its high population has only six (6) landfill sites compared to the one hundred and fifty-five (155) in New Zealand as at 2002. Incineration as a form of waste by a previous administration failed in Lagos apart from the accompanying release of pollutants into the atmosphere.

Waste minimization through recycling is a process of minimizing the quantity of materials that require final disposal. Recycling is not a total cure and solution for solving waste problems but the advantages outweigh the disadvantages in many ways which includes the creation of secondary wastes. It is to be noted however that virtually every type of waste is harnessed in China and Japan from human and animal waste to human hair, animal bones and urine as reported by the Guardian newspaper and Soile et.al [3,4,5].

Projects derivable from wastes include but are not limited to butane gas extraction subject to the availability of harvesting equipment and packaging, conversion of food and plant wastes considering the fruit and other markets and the ready availability of investors for generating electricity from the various transfer loading stations. Worthy of note is the use of agricultural wastes such as rice husk and ground shell which are burnt in a kiln to produce energy by the Cement Company of Northern Nigeria a far back as 2006 to bring down heavy fuel cost by 10% and invariably the production cost and cost of cement. The company is giving consideration to sawdust and cotton lint which are in abundance and constituting a menace.

This study focuses on the energy recoverable from non-hazardous municipal solid waste as a viable method of waste disposal using the thermochemical liquefaction process.

The pioneering "oil from refuse" process was developed by Chemists at the University of Manchester Institute of Science and Technology with a substantial cash backing from the Greater Manchester County Council. In simple terms the process turns everyday household rubbish and biomass products like plant life and vegetation into oil nearly as good as typical petroleum crude oil.

Lagos as a pace setter in waste management in Nigeria should be able to replicate its achievement in other parts of the country and the sub-region if all the on-going efforts are properly harnessed with the integration of this thermo chemical liquefaction of biomass process into the integrated solid waste management project.

This is to all intents and purposes a practical venture which will not only contribute to solving waste disposal challenges but with value added to manufacturers who will use the produced oil as a cheaper energy source in their operations.

Against this background, this study aims to investigate the effects of temperatures at constant H<sub>2</sub>, CO, N<sub>2</sub> pressure and under vacuum as well as that of H<sub>2</sub>, CO, N<sub>2</sub> pressure and under vacuum at constant temperature of 300°C, 350°C or 375°C in making oil using Ru/Al<sub>y</sub>(SiO<sub>4</sub>)<sub>x</sub> catalyst as previously reported by Soile and Owoyokun [8]. The effects of varying and keeping temperatures constant at different atmospheric conditions of 40 atm H<sub>2</sub>, CO, N<sub>2</sub> and under vacuum obtained at 20 mmHg on 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.

## Materials and methods

The biomass feed used in the study was 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. The feed was characterized to ascertain its elemental and moisture composition. The suspension medium, tetralin (3,4 tetrahydronaphthalene) supplied by Huls Limited was used as organic solvent. Six (6) different Ruthenium and Nickel catalysts have been reported in the literature but Ru/Al<sub>y</sub>(SiO<sub>4</sub>)<sub>x</sub> a ruthenium supported, greyish black spherical pellets obtained from Johnson Matthey Research centre, UK is used as a representative sample in this study as previously reported by Soile et al [7,8,9,10,11,12,13]. 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 pressurized 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 40 atm effected with H<sub>2</sub>, CO as reductants, N<sub>2</sub> provided an inert atmosphere and some reactions were 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.

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

(ii) H/C atomic ratio was calculated viz:  $\frac{\%H}{1.008} / \frac{\%C}{12.01}$

(iii) O/C atomic ratio was calculated viz:  $\frac{\%O}{1.008} / \frac{\%C}{12.01}$

(iv) % Oil Yield, %Y =  $\frac{gC_{in\ oil}}{gC_{in\ feed}} \times 100$

(v) %CHR measures the mass of carbon and hydrogen which was recovered as part of an oil product from a given mass of original feed viz:

$$\%Y = \frac{gC_{in\ oil}}{gC_{in\ feed}} \times 100 \dots(1)$$

$$\% C + H = \frac{gC + gH}{g_{oil}} \times 100 \dots\dots\dots(2)$$



$$\% \text{ CHR} = (1) \times (2)$$

$$\% \text{ CHR} = \frac{g_{\text{Cin oil}}}{g_{\text{Cin feed}}} \times 100 \times \frac{g_{\text{C}} + g_{\text{H}}}{g_{\text{oil}}} \times 100$$

$$\% \text{ CHR} = \frac{g_{\text{C}} + g_{\text{H}}}{g_{\text{Cin feed}}} \times 100$$

$$(vi) \quad \% \text{ Conversion, } \%X = \frac{g_{\text{Cin feed}} - g_{\text{Cin char}}}{g_{\text{Cin feed}}} \times 100$$

Product oil parameters namely, percentage yield (%Y), percentage conversion (%X), percentage carbon and hydrogen recovered as oil (%CHR), H/C and O/C atomic ratios were determined from the analysis of the oil obtained. The values of these parameters were subjected to statistical analysis using analysis of variance (ANOVA) at 5% significance level. Post Hoc test using Turkey was used to ascertain the direction of the variance. The schematic diagram [8] of the thermochemical liquefaction of Kraft lignin is shown in fig.1.

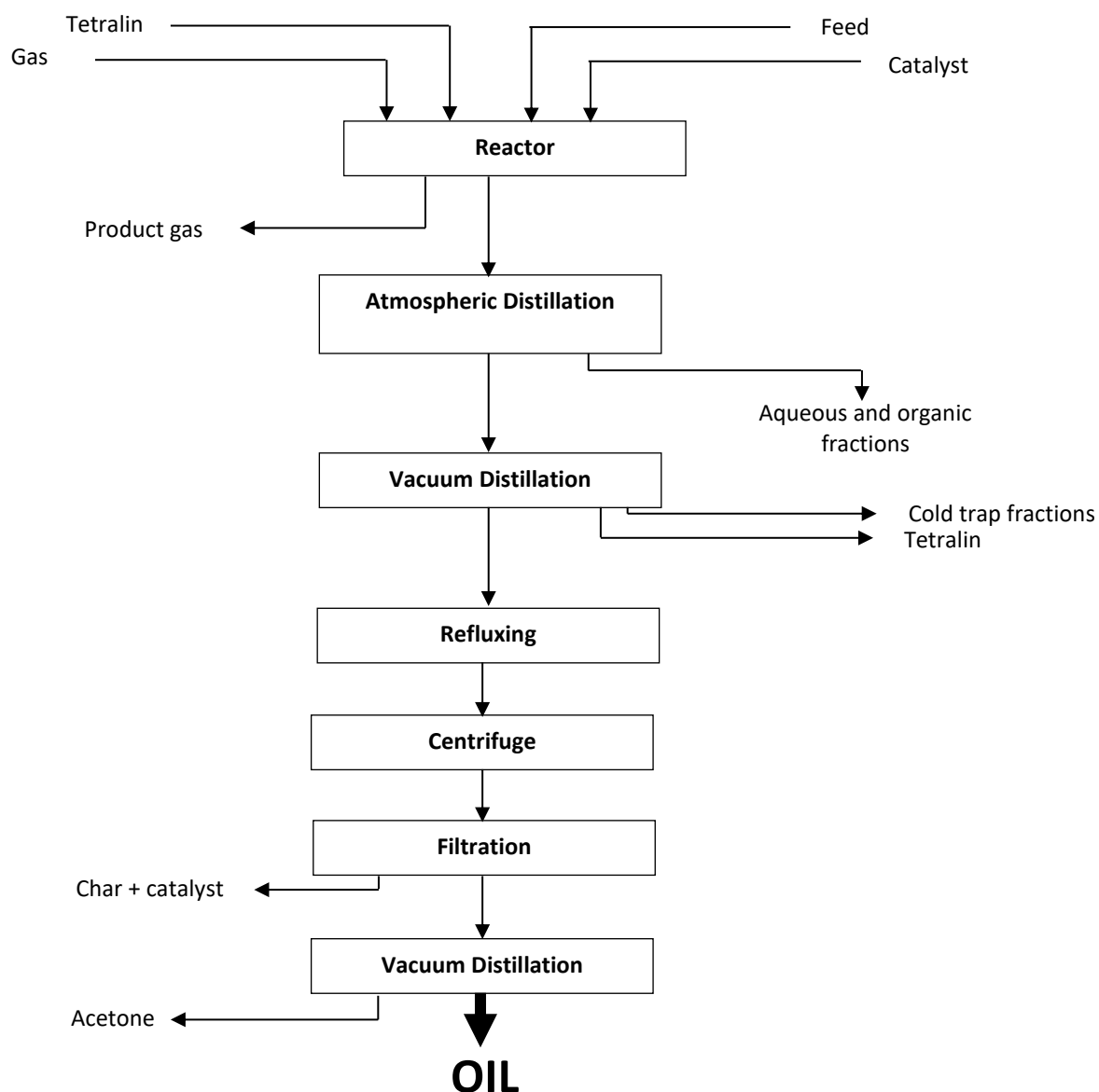


Figure 1: Schematic Diagram of the Liquefaction of Kraft-Lignin [ 8 ]

## Results and discussion

**Analysis of feedstock:**

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

**Table 1: Characterization of the Feedstock**

Parameters	% Moisture	%C	% H	% N	%O	%S	%As h	H/C ratio	O/C ratio
Amount	4.0	58.8	5.7	1.4	28.5	2.4	3.2	1.16	0.36

**Table 2: Trace metal Analysis of feedstock**

Element	Na	K	Mg	Ca	Fe
Amount %	1.0	0.1	0.02	0.1	0.1

**Effects of varying atmospheric conditions at fixed Temperature and varying Temperature at fixed atmospheric conditions:**

The effects of varying atmospheric conditions at fixed 300, 350 and 375°C respectively and varying temperature at fixed hydrogen, carbon monoxide, nitrogen and vacuum atmospheric conditions respectively on the oil produced from the liquefaction of Kraft lignin are presented in tables 3a,3b,3c,4a,4b,4c and 4d. Both atmospheric condition and temperature variables were at constant pressure of 40 atm. except the reactions carried out under vacuum condition of 20mmHg.

The highest desirable parameters were obtained at 375°C and the lowest at 300°C while vacuum atmosphere provided the best atmospheric condition for the best quality and oil quantity from all the tables [8].

**Table 3a: Effects of Varying Atmospheric Conditions at Fixed Temperature**

	Temperature (300°C)			
	H <sub>2</sub> (40atm)	N <sub>2</sub> (40atm)	CO (40atm)	Vacuum(20mmHg)
%Y	56.00±0.05	69.60±0.05	76.40±0.05	56.20±0.05
%X	51.90±0.05	48.20±0.08	57.70±0.05	58.60±0.05
%CHR	36.80±0.01	44.50±0.06	49.00±0.05	36.10±0.03
H/C ratio	1.40±0.01	1.05±0.05	1.07±0.02	1.08±0.02
O/C ratio	0.20±0.01	0.15±0.05	0.16±0.03	0.17±0.02

**Table 3b: Effects of Varying Atmospheric Conditions at Fixed Temperature**

	Temperature (350°C)			
	H <sub>2</sub> (40atm)	N <sub>2</sub> (40atm)	CO(40atm)	Vacuum(20mmHg)
%Y	57.30±0.05	71.20±0.05	64.60±0.05	78.90±0.04
%X	56.30±0.04	57.00±0.40	57.20±0.01	66.00±0.50
%CHR	36.80±0.02	45.50±0.05	41.30±0.05	50.80±0.04
H/C ratio	1.08±0.02	1.04±0.06	1.06±0.04	1.12±0.03
O/C ratio	0.15±0.02	0.13±0.02	0.13±0.01	0.18±0.03

**Table 3c : Effects of Varying Atmospheric Conditions at Fixed Temperature**

	Temperature (375°C)			
	H <sub>2</sub> (40atm)	N <sub>2</sub> (40atm)	CO(40atm)	Vacuum(20mmHg)
%Y	58.20±0.05	94.00±0.50	81.70±0.05	94.30±0.05
%X	61.70±0.02	66.60±0.04	71.30±0.05	75.60±0.01
%CHR	37.70±0.05	59.60±0.02	52.40±0.04	60.50±0.05
H/C ratio	1.22±0.03	1.18±0.04	1.07±0.04	1.09±0.02
O/C ratio	0.10±0.04	0.11±0.05	0.11±0.01	1.09±0.02

**Table 4a: Effects of Varying Temperature at Fixed Atmospheric Conditions**

	Reductant - H <sub>2</sub> (40atm)		
	300°C	350°C	375°C
%Y	56.00±0.05	57.30±0.05	58.20±0.05
%X	51.90±0.05	56.30±0.04	61.70±0.02
%CHR	36.80±0.01	36.80±0.02	37.70±0.05
H/C ratio	1.40±0.01	1.08±0.02	1.22±0.03
O/C ratio	0.20±0.01	0.15±0.02	0.10±0.04

**Table 4b: Effects of Varying Temperature at Fixed Atmospheric Conditions**

	Reductant – CO (40atm)		
	300°C	350°C	375°C
%Y	76.40±0.05	64.60±0.05	81.70±0.05
%X	57.70±0.05	57.20±0.01	71.30±0.05
%CHR	49.00±0.05	41.30±0.05	52.40±0.04
H/C ratio	1.07±0.02	1.06±0.04	1.07±0.04
O/C ratio	0.16±0.03	0.13±0.01	0.11±0.01

**Table 4c: Effects of Varying Temperature at Fixed Atmospheric Conditions**

	Inert Atmosphere - N <sub>2</sub> (40atm)		
	300°C	350°C	375°C
%Y	69.60±0.05	71.20±0.05	94.00±0.50
%X	48.20±0.08	57.00±0.40	66.60±0.04
%CHR	44.50±0.06	45.50±0.05	59.60±0.02
H/C ratio	1.05±0.05	1.04±0.06	1.18±0.04
O/C ratio	0.15±0.05	0.13±0.02	0.11±0.05

**Table 4d: Effects of Varying Temperature at Fixed Atmospheric Conditions**

	Vacuum (20mmHg)		
	300°C	350°C	375°C
%Y	56.20±0.05	78.90±0.04	94.30±0.05
%X	58.60±0.05	66.00±0.50	75.60±0.01
%CHR	36.10±0.03	50.80±0.04	60.50±0.05
H/C ratio	1.08±0.02	1.12±0.03	1.09±0.02
O/C ratio	0.17±0.02	0.18±0.03	0.09±0.02

### **Other important Observations in the Results:**

Comparing the H/C and O/C ratios obtained in the feedstock and the product oil; the decrease in the H/C and O/C atomic ratios relative to those of the feedstock could be attributed to the increased production of carbon monoxide and carbon dioxide in the reactions. The amount of aqueous fractions produced is 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. Removal of water in this study has not been an efficient way of reducing oxygen content. Probably the most important overall reaction in converting the lignin material to oil is the splitting out of oxygen to form molecules with higher H/C and lower O/C atomic ratios. Lignin loses water and carbon dioxide on being heated. Oxygen can also be lost by reaction with the added carbon monoxide to form carbon dioxide by hydrogenation, disproportionation or by a combination of these reactions which would result in an oil made up of a complex mixture of different compounds. Replacing carbon monoxide with hydrogen did not have any appreciable effect on conversion and other quality parameters and therefore it may be more economical to use synthesis gas instead of pure carbon monoxide or hydrogen in the initial charge to the autoclave. Though the objective of low O/C atomic ratio has been attained but increasing the H/C atomic ratio relative to the starting material did not materialize fully.

Product oil fluidity were also visually observed to decrease with rise in temperature but oils produced using carbon monoxide as reductant were less viscous than those produced in the atmosphere of vacuum, nitrogen and hydrogen. This observation may be of some importance if the oil is to be used directly as a fuel oil. However if it is to be further upgraded a more viscous oil could be a suitable intermediate.

Possible catalytic contribution of trace metals in the feed could also result in increased conversion. At the same time these inorganic elements can be superimposed on the effects of other important factors such as catalyst poisoning.

### **Conclusion**

The experiments conducted in this study have provided some basic information in the thermochemical liquefaction of Kraft lignin and as a means of converting biomass including municipal waste into valuable oil products and other chemicals and therefore another solution to waste disposal problems. Its use of water as slurry solvent as reported by Soile [10] has shown it to be a very effective suspension medium which means feedstock drying especially of municipal waste/refuse and solvent recovery are unnecessary thus reducing capital cost. The penalty will however be in the high capital cost of high pressure equipment that will be required to withstand high pressure.

The char from the process could be used for land filling, filler for plastics or upgraded to provide a rich source of activated carbon.

The oil produced can be used directly to power mills and its unlike petroleum derived oil with its much higher oxygen content and phenolic material Comparison of its energy values with the conventional crude showed a gap as reported by Soile [8].

The oil will therefore make a considerable in road into the petrochemical industry as a chemical feedstock after further characterization and upgrading.

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### Conflict of Interest:

The authors declare that there are no competing or conflicting interest.

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