Characterization of products of Thermochemical Liquefaction of Kraft Lignin using 3%Ru/Aly(SiO4)x Catalyst.

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ABSTRACT: The thermo chemical liquefaction of Kraft Lignin was carried out using 3% Ru/Aly (S104)X catalyst at 350oC in different atmospheric conditions at 2 hours reaction time to produce a mixture gaseous, liquid and charry products which are all capable of use as fuels and chemicals. The product gases were quantified using the well known gas equations and identified qualitatively by infrared spectroscopy and gas chromatography. The chars were characterized by elemental analysis. The liquid product obtained after atmospheric and vacuum distillation was separated into various fractions by solvent extraction and column chromatography. These fractions were subsequently characterized by elemental analysis, gas-liquid chromatography – mass spectrometry, high performance liquid chromatography, infrared spectroscopy and 13C nuclear magnetic spectroscopy.

Key words: Thermochemical, liquefaction, fractionation, characterization spectroscopy, chromatography.

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INTRODUCTION:

Lignin is a major component of biomass [1, 2, 3, 4] and the liquefaction of Kraft Lignin has been shown to be important for the potential production of fuel, inorganic and hydrocarbon gases, chars and liquids which are all sources of petrochemical feedstocks [3, 4] Product gases include methane, ethane , propane, sulphide gases carbon monoxide and carbon dioxide. Carbon dioxide can find important outlet in the distillery industry and the hydrocarbon gas mixture can provide a source of energy for the process after carbon dioxide scrubbing. The chary product could be upgraded to activated carbon which has industrial applications as well as being used for land filling or as a filler for plastics.

In the study, however, emphasis is placed on the liquid products hereinafter referred to as oils. These oils are very complex mixtures containing oxygenated hydrocarbons and differ from the natural crude oils which basically contains hydrocarbons (5,6).

The conversion of biomass materials into oils generally has a precise objective which is to transform a carbonaceous solid materials which is originally difficult to handle, bulky and of low energy concentration into pumpable oils having physicochemical characteristics and which permit storage transferability through pumping systems and for further use either in direct combustion furnaces or as feedstock for hydro treatment leading to specific fuels and chemicals (3). An approach based on a combination of both solubility and acid base properties of biomass in is somewhat more useful, for example, a major part of biomass oil can be extracted from chloroform into aqueous sodium hydroxide but not bicarbonate, thus revealing the predominantly phenolic character of these materials. In practice, however, aqueous extraction technique based on the acid-base properties have proved to be of limited utility [7].

A good deal of information regarding the structural characteristic has been obtained by gc-ms technique and further progress along than line will be difficult for two reasons.

First, even with high resolution afforded by capillary GC there is the general problem of overlapping peaks that plagues analysis of extremely complex mixtures. The second limitation is that 30% or more of the biomass oil is usually too involatile to be analysed by gas chromatograph.

There seemed to be a need, therefore for an approach that would fill the gaps left by gc –ms techniques for characterization of biomass oil. The ideal method would be fairly sample, rapid, reproducible and capable of separating these materials into classes according to chemical functionally.

The scope of this study is to report a simple, rapid and reproducible method which could be used to fractionate the oils into various identifiable fractions and to be used to compare the outfall of several experiments. The experimental procedure used to obtain the gaseous, liquid and Charry products have been reported elsewhere in the literature [8,9,10,11]. A mass balance was carried out for each

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reaction in order to establish whether mass was effectively conserved so as to be able to assess the economic viability or otherwise of the process.

Experimental:

Products recovery were carried out as detailed in previous reports[10,11]

Gases:

The product gas was a mixture of gases and volatile organic compounds generated by the reaction. The gases were vented at room temperature and a gas storage system comprised of a vacuum pump, several pre-evacuated glass bulbs of known volumes and an in -line nitrogen cold trap. The pressure reading on the manometer was taken before and after venting out the gases. The volume of the gas was reduced to standard temperature and pressure. The weight and molecular weight of gaseous products were determined by using the well known gas equations.

Product Gas Analysis: By Infrared Spectroscopy

Samples of the gaseous products for all the reactions were collected in a 10cm path length glass cell with sodium chloride windows and analyzed with a Perkin–Elmer 157 Spectrotophotomer having a range of 600-4000cm^{-1} Identification was aided with a number of standard gases and gas mixtures and the spectra were correllated with those in the literature.

Gas Analysis by gas chromatography

A Pye Unicam server 204 gas chromatography coupled to a Hewlett Packard data dynamic 390 was used. The chromatography has a dual detector system comprising the katharometer (Thermal conductivity) and flame lionization detector, the flame was used for CO and CO2 while the later was used for the hydrocarbon gases. H_2S was analyzed separately on another Pye Unicam series 204. Fitted with a flame photometric detector and linked to the same data processing unit. Gas injection was by means of a gas loop fitted with a mercury manometer. A PTFE column (3mX 4mm rod) packed with Porapak QS 80/100 mesh was used.

The set of conductions used for the analyses of CO, CO_2 and the hydrocarbon gases were different from those of the H_2S.

To aid identification of the components of the gaseous products, the gas chromatography was calibrated with authentic samples of gases considered to be the likely components of the gaseous products. This afforded the retention times and response factors of these gases.

The calibration gases were methane, ethane, ethylene propane, propylene, C0, $C0_2$ and H_2S.

The response factor was obtained by plotting gas sample concentration (ml) against peak area count and the gradient was found.

The product gases were identified by comparison with the retention times of the authentic simples used for the calibration.

However some minor components and could not be identified because of the unavailability of authentic gas samples which could have been used at the time of the study.

However, H_2, was not identified because of the Porasil type column and the detector system used [12]. H_2, C0, $C0_2$, are not normally detected by the FID. H_2 was nonetheless approximated as follows:

% H_2 = (100 –Total % of all identified components).

A standard of mixture was analysed from time to time to ensure reproducibility of results and to test the effectiveness of this method of analysis.

Product Oil Analysis

The elemental analysis, char ,oil yield and conversion were determined as previously reported [10,11].

Tetralin determination in the product oil

Tetralin (1,2, 3, 4 Tetrahydronaphthalene) was used as the solvent in all the liquefaction processes and was determined with a Carlo Erba Fractovap 2150 series with an electrometer model 180, a temperature programmer model 232 gas chromatograph fitted a flame Ionization detector using the internal standard technique. Integration was by a Hewlett –Packard integrator model 3390 A. A soda lime glass column (30m X 0.2mm i.d) packed with methysilicones was used.

Analysis of the light volatiles from distillation.

The organic fractions from the atmospheric and vacuum (cold trap) distillation were analyzed for their elemental constituents and the infrared spectrum of each fraction was also taken to help in the identification of these fractions.

Gas chromatographic analyses of these fractions involved the use of the Pye Unicam chromatograph series 204 fitted with flame Ionization detector and coupled to a data processing Hewlett-Packard data dynamics 390. Identification was achieved by further analysis using the gc-ms technique. A Pyrex glass column (1.5mm X 2mm i.d) packed with 3%Ov 17 80/100 mesh was used.

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Analysis of oil by simple solvent extraction

The method used was based on the Institute of Petroleum Standard method IP 143-78 [13] with some modification. This method has wide applications to crude oil, gas oil, diesel fuel, lubricating oil and bitumen.

The product oil in this study was separated into resins, asphaltenes and light volatiles using ethyl acetate, toluene and heptane respectively.

Separation of resins: A known weight of oil was weighed accurately in a round bottom flask. Ethyl acetate (BDH Chemicals – GPR) was added in the ratio of 40ml to each gram of oil sample. The mixture was boiled under reflux for two hours on a heating mantle. A boiling chip was added to prevent the mixture from bumping or boiling over. After the reflux, the heating mantle was switched off and the flask and its contents were allowed to cool. Without agitation, the solvent (now coloured)

was decanted through a filter paper Whatman No. 1 under water vacuum. The residue on the filter paper was washed with successive quantities of ethyl acetate. The ethyl acetate insoluble residue, dark brown in colour, hereafter referred to as resins, was dried overnight in an oven at 100^{0}c. it was later cooled in a dessicator and its weight obtained by difference. It was analysed for its elemental constituents.

Separation of the asphaltenes and light volatiles: The ethyl acetate filterate from the above was stripped of its solvent on a rotary evaporator under water vacuum leaving a dark brown oily residue. Heptane was added to this residue in the ratio of 40ml to each gram of residue and boiled under reflux for two hours. After the reflux, the mixture was allowed to cool and separated on a Whatman No. 1filter paper under vacuum. The heptane insoluble residue, hereafter referred to as the asphaltenes, stuck to the sides of the flask and was washed with successive quantities of heptanes and filtered. The asphaltenes, black brittle solid, were dried in an oven at 100^{0}c and later cooled in a desiccators. The combined heptane filtrates was stripped of its solvent on a rotary evaporator to obtain a viscous yellowish liquid, hereafter known as the light volatiles. The weights of the asphaltenes and the light volatiles were obtained by difference.

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Elution column chromatography

Attempts were made to separate the light volatiles into saturates, aromatic and polar fractions by elution column chromatography. The method used was preferably a physical one for separating aromatic and non-aromatic fractions of high boiling oil

Analytical grade heptane, toluene and methanol were used in this elution column chromatography. The column packing materials were made up of chromatographic grade silica gel adsorbent (100-200 mesh, BDH Chemicals) and alumina adsorbent (100-200 mesh, active, neutral, pH 6.5-7.5, BDH Chemicals), nitrogen gas dried over molecular sieve type 3x and delivered to the top of the column at a regulated flow rate served as the pressuring gas.

The infrared spectrum of each fraction was taken to verify separation into the following groups:

(I) Saturates – pale yellow mobile liquid.

(II) Aromatic – and (iii) Polar compounds which were black and very viscous liquids.

The complex and viscous nature of the aromatic and polar fractions rendered them less amenable to glc analysis. Attempts were however made to analyze these fractions by glc using the Pye Unicam series 204 gas chromatograph.

Analysis of oil by Continuous Solvent Extraction

The method employed in this work is an adaptation of the sequential elution by solvents chromatography developed by Farcasiu[14] for separating coal fluids into distinct chemical classes. This continuous extraction technique is meant to be fairly simple, rapid, reproducible and capable of separating the oils produced in this study into classes according to chemical functionality using analytical grade heptane ,toluene ,chloroform ,methanol and ethanol.

The heptane and toluene extracts were pale yellow liquids, the chloroform extract was a dark coloured very viscous liquid, the ethanol extract was a semi-solid gummy material while the methanol extract and the residue were solid materials. Infrared spectrum and the elemental analysis of each fraction were considered to establish if the separation had been successful. The heptane and the toluene extracts were analyzed by glc using the Pye Unicam series 204 chromatograph. The GC-MS technique was also used in the identification of the components of these fractions.

High Performance Liquid Chromatography

The chloroform, ethanol and methanol extracts were analyzed on a Shimadzu high performance liquid chromatograph LC-4A series which comprises of the hplc LC-4A as the base, solvent delivery unit of ternary gradient capability, processor with a microcomputer, Shimadzu chromatopac C-RIB recorder and ultra violet

spectrophotomeric detector, SPD-2AS with a D_2 source lamp. The hplc was used because of the nature of the extracts which does not make them amenable to glc separation.

The sample was dissolved completely in the mobile phase and filtered otherwise undissolved sample gradually dissolves at the column inlet, to prevent tailing of peak and drift of base line and clogging of the column. Immiscible substances were removed by filtration. The sample was then introduced into the column by a syringe loop injector.

Determination of Aromatic Content of Oil Using ^{13}C n.m.r.

The aromatic content of the product oil and separated fractions was determined using the ^{13}C n.m.r.

Sample of the oil or the separated fraction and 50 mg of chromium tris acetylacetonate, $Cr(acac)_3$ was added to 1 ml of deuterated acetone containing about 1% tetramethy1 silane as a chemical shift reference standard in a sample tube of 5mm in dimension. Data acquisition time was 1.023 seconds after each 1200 pulses with a time delay of 2 seconds between the end of data acquisition and the beginning of the next pulse. The proton spin decoupler was gated off during the delay. The regions were integrated two or three times and the results were averaged. This 100-170 ppm integral was expressed as a percentage of the total integral. Spectrum width was 200 ppm.

Gas Chromatographic-Mass Spectroscopic Analysis of the Oil

To aid the identification of the major components which are subjected to glc separation, the previously obtained fractions were analyzed by using the gas chromatography-mass spectrometry (GC-MS) technique at the pre-determined glc conditions. The technique involved a gas chromatographic equipment coupled to a

mass spectrometer through an interface that enriches the concentration of the sample in the carrier gas. The techniques measured the relative molecular masses with very accuracy and from which can be deduced the exact molecular formulae. The electron impact ionization (EI) technique was used in the study.

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RESULTS AND DISCUSSION

Tables 1a,1b,2a,2b,3a,3b,4a and 4b details information on reaction inputs and parameters,products recovery after processing,product gas recovery and distribution and products distribution.This gives an indication of mass conservation.

Table 1a: Reaction Inputs and Parameters

Run	10	11	12	35	36	37	38	42	43	44
Feed (g)	50	50	50	50	50	50	50	50	50	50

Tetrain (g)	400	400	400	400	400	400	400	400	400	400
Reductants	N_2	H_2	CO	H_2	CO	CO	CO	-	H_2	H_2
Gaseous Input (g)	23.7	1.7	23.7	1.7	1.7	23.3	23.4	-	0.8	2.6
Catalyst Input (g)	1.00	1.10	1.10	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Rxn. Temp (^oC)	350	350	350	300	375	300	375	375	350	350
Heat Up Time (Hr)	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Rxn Time (Hr)	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Initial Rxn Pres (alm)	40	40	40	40	40	40	40	0	20	60
Max Rxn Pres (atm)	115	115	115	100	130	90	128	58	79	160
Final Rxn Pres (alm)	40	40	40	40	42	38	42	0	20	58
Total Input(g)	474.8	452.8	474.8	452.7	452.7	474.3	474.4	451.0	451.8	453.6
Total Output (g)	461.6	445.5	463.4	441.3	446.4	459.8	462.2	446.2	447.2	450.2
Recovery (%)	97.2	98.4	97.6	97.5	98.6	96.9	97.4	98.9	98.9	99.2

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Table 1b:Reaction Inputs and Parameters

Run	45	46	67	68	69	74	76	77	78	80
Feed (g)	50	50	50	50	50	50	50	50	50	50

Tetralin (g)	400	400	400	400	400	400	400	400	400	400
Reductant	CO	CO	H_2	H_2	H_2	CO	H_2	-	-	CO
Gaseous Input (g)	11.8	35.8	1.7	1.7	1.7	23.5	1.7	-	-	23.9
Catalyst Input (g)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	-	1.00
Rxn. Temp (^oC)	350	350	350	305	350	350	350	350	350	350
Heat Up Time (Hr)	1.35	1.35	1.40	1.35	1.35	1.35	2.00	2.00	2.00	2.00
Rxn Time (Hr)	2.00	2.00	2.00	1.00	3.00	2.00	2.00	2.00	2.00	2.00
Initial Rxn Pres (alm)	20	60	40	40	40	40	40	0	0	40
Max Rxn Pres (atm)	78	158	118	118	118	100	95	18	18	272
Final Rxn Pres (alm)	20	58	42	40	42	39	40	0	0	45
Total Input (g)	462.8	486.8	452.7	452.7	452.7	474.5	402.7	401.0	400.0	474.9
Total Output (g)	456.3	471..9	448.5	448.4	449.5	453.4	396.6	397.2	396.2	454.7
Recovery (%)	98.6	96.9	99.1	99.1	99.3	95.6	98.4	99.1	99.1	95.7

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Table 2: Product Recovery after Processing

Run	Atm Distillation		Vac. Distillation			Char (g)	Oil (g)	*Processing Recovery (%)
	Org fr (g)	Aq. Fr (g)	Solvent Recovery (g)	Cold Trap Aq. Fr (g)	Org fr (g)			
10	1.6	2.5	385.6	1.0	0.2	18.1	27.2	94.5
11	2.9	5.1	388.4	0.6	0.2	18.9	22.1	98.4
12	2.0	3.5	385.8	0.7	0.3	17.7	24.4	93.7
35	0.8	1.3	377.2	5.0	2.3	21.6	25.7	98.3
36	1.8	4.1	388.1	0.4	0.9	15.9	22.5	97.2
37	-	-	380.0	3.8	1.8	18.9	30.1	94.5
38	-	-	385.7	6.6	4.6	12.9	30.4	95.2
42	-	-	375.4	8.0	4.4	12.3	35.3	97.6
43	-	-	384.1	8.5	4.9	15.3	30.3	99.1

44	-	-	380.3	8.9	2.7	17.3	31.9	98.0
45	-	-	368.5	9.6	4.5	21.3	24.4	93.9
46	-	-	378.5	7.0	1.9	18.8	28.2	91.5
67	-	-	385.9	7.9	2.7	18.0	30.1	99.1
68	-	-	377.4	7.9	3.9	17.4	37.3	99.0
69	-	-	381.3	8.1	4.6	16.3	34.5	99.0
74	-	-	383.6	5.0	3.0	17.7	28.5	96.6
80	-	-	372.8	-	-	5.7	26.2	89.0

$$* \quad \% \quad \frac{\text{Total Produced}}{\text{Total input}} \times 100$$

Table 3a: Product Gas Recovery and Distribution

Run	10	11	12	35	36	37	38	42
Volume at stp (L)	18.1	17.4	18.0	16.9	17.1	16.4	18.6	3.2
Mol. Weight (g)	26.7	4.2	28.1	3.9	4.9	27.2	26.2	20.8
Weight (g)	21.5	3.3	22.6	2.9	3.7	19.9	21.7	3.0
Net weight * (g)	-2.2	1.6	-1.1	1.2	2.0	-3.4	-1.7	3.0
% Gas * *	-	3.2	-	2.4	4.0	-	-	6.0
% H_2S	52.4	52.4	61.1	14.3	37.5	71.9	77.0	77.6
% CO	21.1	7.0	18.4	15.4	11.2	12.5	7.7	8.7
% CO_2	0.3	0.2	T***	-	0.1	0.1	0.3	T***
% CH_4	4.6	3.3	4.0	0.2	2.5	0.6	3.5	11.8
% $C_2 H_4$	-	-	-	-	-	-	-	-
% $C_2 H_6$	1.0	0.2	1.2	-	0.3	0.2	1.2	0.8
% $C_3 H_8$	0.5	0.2	0.5	-	0.1	0.1	0.1	0.3
% Total	90.6	63.3	85.2	29.9	51.7	85.4	90.1	99.2
% H_2	9.4	36.7	14.8	70.1	48.3	14.6	9.9	0.8

* Net weight = Wt of gaseous product – wt of gaseous input

** % Gas = $\frac{\text{Net wt of Gaseous Product}}{\text{Wt of feed}} \times \frac{100}{1}$

*** T = < 0.05 %

Table 3b: Product Gas Recovery and Distribution

Run	43	44	45	46	67	68	69	74	80
Volume at STP. (L).	10.1	24.2	10.7	24.7	18.1	18.4	18.1	20.2	26.7
Mol.Weight(g)	5.9	7.5	38.1	28.6	3.7	4.3	4.6	16.2	28.4
Weight (g)	2.7	8.1	18.2	31.5	3.0	3.5	3.7	14.6	33.9
Net weight	1.9	5.5	6.4	-4.3	1.3	1.8	2.0	-8.9	10.0
% Gas **	3.8	11.6	12.8	-	2.6	3.6	3.7	14.6	33.9
% H_2 S	89.5	14.1	80.3	21.2	37.9	64.8	64.9	16.6	62.6
% Co	7.2	0.2	11.8	1o.5	0.9	5.8	0.6	5.9	1.6
% Co_2	T***	T***	0.3	0.2	0.1	0.1	0.1	0.6	0.8
% C H_4	1.7	1.6	1.2	1.5	0.7	4.3	1.7	1.3	0.6
% $C_2 H_4$	-	-	-	-	T***	-	T***	T***	T***
% $C_2 H_6$	0.3	0.2	0.2	0.3	0.2	0.5	0.7	0.5	0.2
% $C_3 H_8$	0.1	T***	T***	0.1	0.1	0.1	T***	0.3	0.1

% Total	98.8	16.1	93,7	33.8	40.9	72.6	68.7	25.2	65.9
% H_2	1.2	83.9	6.3	66.2	59.1	27.4	31.3	74.8	34.1

* Net weight = wt of gaseous product – wt of gaseous input

** % Gas = $\frac{\text{Net wt of gaseous product}}{\text{Wt of feed}} \times \frac{100}{1}$

*** T = 0.05%

Table 4a: Product Distribution

Run	10	11	12	35	36	37	38	42	43
Gaseous product %	-	3.2	-	2.4	4.0	-	-	6.0	3.8
Aqueous product %	7.0	11.4	8.4	12.6	9.0	7.6	13.2	16.0	17.0
Solvent recovery %	96.4	97.1	96.4	94.3	97.0	95.0	96.4	93.9	96.0
Char %	36.2	37.8	35.4	43.2	31.8	37.8	25.8	24.6	30.6
Oil %	54.4	44.2	48.8	51.4	45.0	60.2	60.8	70.6	60.6
Oil yield %	71.2	57.3	64.6	56.0	58.2	76.4	81.7	94.3	74.4
Conversion %	57.0	56.3	57.2	51.9	61.7	57.7	71.3	75.6	64.9
CHR oil %	45.5	36.8	41.3	36.8	37.7	49.0	52.4	60.5	48.9

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Table 4b: Product Distribution

Run	44	45	46	67	68	69	74	80
Gaseous Product %	11.0	12.8	-	2.6	3.6	4.0	-	2.0
Aqueous Product %	17.8	19.2	14.0	15.8	15.8	16.2	10.0	-
Solvent Recovery %	95.1	94.6	94.6	96.5	94.4	95.3	95.9	93.2
Char %	34.6	42.6	37.6	36.0	34.8	32.6	35.4	11.4
Oil %	63.8	48.8	56.4	60.0	74.4	69.0	57.0	52.4
Oil Yield %	81.6	62.2	75.8	73.0	98.4	89.4	72.6	68.0
Conversion %	58.1	49.4	53.3	59.2	58.9	61.9	73.6	84.9

CHR Oil %	52.2	40.1	48.7	46.7	63.3	52.6	47.4	43.6

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Table 5: Oil Fractionation into Light Volatiles , Asphaltenes and Resins

Run	% Light Volatiles	% Asphaltenes	% Resins
10	34.3	58.6	5.5
11.	26.0	69.2	7.1
12.	35.1	60.1	4.8

Table 6: Elemental Characteristics of the Asphaltenes and Resins

Run No.	Asphaltenes						Resins					
	%C	%H	%N	%O	%S	%Ash	%C	%H	%N	%O	%S	%Arch
10.	75.3	6.5	1.4	16.3	0.5	ND	74.0	4.9	2.5	17.2	0.4	1.0
11.	75.3	6.8	1.3	16.7	0.7	0.2	75.8	5.3	2.4	15.3	0.4	0.8
12.	75.2	6.4	1.4	16.9	0.1	0.1	74.9	4.9	2.4	16.2	0.1	1.5

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Table 7a: Elemental Characteristics of Solvent Extracts

Run	Extract	%C	%H	%N	%O *	%S	%Ash
10		71.2	7.5	0.3	16.3	ND	4.7
11	H	66.2	9.0	0.4	22.0	0.2	2.2
12	E	70.8	7.1	1.2	20.9	ND	ND
42	P	71.8	6.9	0.3	20.2	0.1	0.7
43	T	72.1	7.6	1.2	15.5	0.4	3.2
44	A	75.2	7.6	0.5	16.3	0.2	0.2
67	N	75.2	7.8	0.4	16.0	ND	0.6
69	E	55.4	5.2	0.3	38.9	ND	0.2
74		73.5	8.7	0.4	16.7	0.2	0.5
80		63.8	7.3	0.3	27.0	0.2	1.4
10		71.6	7.1	0.3	19.3	ND	1.7
11	T	72.1	6.9	0.5	20.4	0.1	ND
12	O	55.0	6.1	0.1	38.8	ND	ND
42	L	72.3	7.2	0.6	19.8	0.1	ND
43	U	74.0	7.7	0.4	17.4	0.3	0.2
44	E	77.9	7.3	0.8	13.6	0.1	0.3
67	N	72.3	6.7	0.3	20.7	ND	ND
69	E	74.5	7.2	0.6	17.0	0.3	0.4
74		72.7	6.9	0.5	19.2	0.4	0.3
80		70.4	6.6	0.7	21.1	0.2	1.0
10	C	75.7	7.6	0.7	15.5	0.5	ND
11	H	75.8	6.9	0.7	16.1	0.2	0.3
12	L	72.7	7.6	0.5	18.8	ND	0.4
42	O	76.7	7.3	0.9	14.5	0.4	0.2
43	R	76.1	7.3	0.8	15.2	0.2	0.4
44	O	76.0	7.3	1.0	14.8	0.2	0.7
67	F	75.6	6.7	0.6	15.6	1.2	0.3
69	O	73.6	7.1	ND	18.7	0.4	0.2
74	R	73.7	7.1	0.9	18.0	0.2	0.1
80	M	71.5	7.2	0.9	20.2	0.2	ND

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Table 7b: Elemental Characteristics of Solvent Extracts

Run	Extract	%C	%H	%N	%O *	%S	%Ash
10		71.4	6.3	1.1	21.1	ND	0.1
11	E	74.0	5.6	1.8	18.2	0.4	ND
12	T	74.5	6.0	1.2	17.9	ND	0.4
42	H	75.3	6.6	1.6	16.1	0.3	0.1
43	A	72.6	6.5	1.3	19.1	0.3	0.2
44	N	75.5	6.1	1.5	15.5	0.3	0.1
67	O	73.2	6.5	1.3	18.9	ND	0.1
69	L	73.1	5.8	1.4	19.4	0.2	0.1
74		70.5	6.3	1.7	20.2	ND	1.3
80		75.7	5.3	1.5	16.9	0.6	ND
10		69.8	6.2	1.3	20.2	0.3	2.2
11	M	72.0	8.4	1.6	15.5	0.3	2.2
12	E	70.8	7.1	1.2	18.7	0.6	1.6
42	T	73.0	6.7	1.7	16.7	ND	1.9
43	H	70.4	6.1	1.5	21.3	0.2	0.5
44	A	72.3	6.3	1.7	17.7	0.8	1.2
67	N	71.1	6.1	1.3	19.8	0.3	1.4
69	O	71.7	5.8	1.5	19.0	0.3	1.7
74	L	66.8	6.7	1.8	24.2	0.3	0.2
80		67.3	7.5	1.2	20.0	0.1	3.9
10		74.0	4.9	2.2	16.8	0.4	1.7
11	R	73.8	5.0	2.2	18.6	0.4	ND
12	E	71.8	4.6	2.1	19.4	0.8	1.3
42	S	74.7	4.4	2.4	18.5	0.4	1.6
43	I	73.9	4.8	2.2	18.0	0.6	0.5
44	D	75.2	4.6	2.1	18.1	ND	ND
67	U	74.3	5.2	2.3	15.6	0.4	2.2
69	E	74.8	4.8	2.5	17.5	0.2	0.2
74		71.5	5.6	2.4	17.2	ND	3.3
80		74.3	5.3	1.7	17.7	ND	0.1

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Table 8: Elemental Characteristics Of the Light Organic Fractions

Run	%C	%H	%N	%O *	%S	%Ash
10[1]	86.6	9.3	0.3	3.4	ND	0.4
11[1]	8.0	8.6	0.3	11.1	ND	ND
12[1]	87.9	9.4	0.2	1.7	ND	0.8
36[1]	85.6	8.3	0.3	4.9	0.1	0.8
36[2]	87.4	8.9	0.2	1.6	ND	1.9
43[2]	90.1	9.4	0.2	0.1	0.2	ND
44[2]	87.2	9.0	0.1	3.3	ND	0.4
67[2]	89.4	10.4	0.2	-	ND	ND
69[2]	89.2	10.3	0.3	3.4	ND	0.4
80[3]	3.0	11.5	0.3	85.2	ND	ND

*Estimated by difference ND = Non- Detectable
1: Atmospheric distillation
2: Cold trip fraction
3: Aqueous fraction

The ^{13}C measurement the aromatic content was carried out for two oils produced including the chloroform extract of one of the oils.

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Table 9: Reaction carried out at 350°c at 2hrs reaction time

Pressure	Reductant	%Aromatic
Vac	Vac	69.0
40	H_2	51.0
Vac	$CHCl_3$ Vac extract	71.0

Table 9 showed that the aromatic content of the oil produced for two reactions are 69°/₀ and 51°/₀ respectively. The aromatic content of the chloroform extract was slightly higher to 71°/₀ .

Shoolery et al (16) obtained lower aromatic content in their of analysis of crude petroleum using ^{13}C method. The higher values obtained might not be unconnected with the aromatic nature of the feedstock which is made up of phenyl propone moieties. This potentially rapid and accurate measurement of the percentage of the

aromatic carbons in the lignin derived oils is an attractive application and then aromatic content is of special values in many crude oil applications e.g. gasoline where a higher aromatic content corresponds to a higher anti knock quality.

In environmental work, the polycyclic aromatic hydrocarbons are suspected of carcinogenic activity and they are under widespread study.

The assumption of the ^{13}C method in the all ^{13} carbon nuclear regardless of their molecular environment have the same absorption coefficient.

OILS FRACTIONATION AND ANALYSIS

Previous work showed that the crude oil produced from kraft lignin is a viscous liquid that looks like heavy fuel oil and that it has very little in common with crude petroleum. The standard methods of petroleum chemistry are therefore largely inapplicable. There is a need for new methods for the fractionation of biomass oil into constituent chemical classes for the purpose of assessing comparative product quality and evaluating upgrading option and the best end uses.

Many investigators have used ether solubility of the hydrogenation products as the criterion of success without properly considering the nature or separability of individual compounds of the product mixtures. Since ether solubility is characteristic of many materials of relatively high molecular weight, it does not necessarily follow that useful low molecular weight materials will be found if the hydrogenation mixture can be solubilized in ether. Other approaches to the problem of the chemistry of biomass oil include solvent extraction, gc – ms, hplc – ms and adsorption chromatography. Solvent extraction schemes are in common use in the characterization of synthetic fuels including those derived from biomass(17) Biomass oil is more commonly taken as the acetone, chloroform or benzene soluble product and would in the parlance coal fluid chemistry be classified as a mixture of asphaltenes and pre-asphaltenes.

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Separation into Heptane soluble, Asphaltenes and Resins

The composition of oil samples were studied by solvent extraction into light volatiles (heptane solubles) asphaltenes (toluene solubles) and resins (ethyl acetate solubles).

The product distribution is given in table 5 and the elemental characteristics of the asphaltenes and resins are given in table 6.

Asphaltenes are highly condensed polyatomic hydrocarbons while resins are polycondenced heterocyclic hydrocarbons. Asphaltenes could generally be hydrogenated to produce the resins with a good hydrogenation catalyst. The generally high asphaltic content of the oils analyzed clearly indicated the need for a suitable cracking catalyst it better quality oils are to be obtained.

The light volatile fractions accounted for about 20% of the product oils on the average while asphaltenes and resins accounted for 75% and 5% on the average respectively.

The resins contained a higher amount of oxygen, sulphur, nitrogen and ash than the asphaltenes.

The light volatiles were separated into heptane, toluene and methanol fractions by elution column chromatography and analysed by infrared spectroscopy and gas chromatography.

All typical absorptions expected for saturated hydrocarbons have been masked except that the typically weak tetralin absorption at 690 cm in more intense in that region.

Thus absorption is typical of C –H out of plane bending of mono-substituted benzene derivatives. The absence of O –H absorption confirms the absence of phenols, alcohols and carboxylic acids.

The spectrum of the toluene fractions showed all typical absorptions due to toluene except for the intense broad absorption at ca. 800 cm^{-1} which could be due to C –H bending vibration of unsaturated hydro carbons.

The presence of O –H absorption, absorption characteristic of carbonyl compounds and the strong absorptions at 740 cm^{-1} confirms the presence of aromatic carbonyl compounds, alcohols or phenols.

The spectrum of the methanol fraction have the following absorptions present (i) O –H –O stretching due to intermolecularly hydrogen bonded compounds at ca. 3400 cm (ii) C –H stretching due to CH_3ca. 2850 cm^{-1}, (iii)$^{o-H}$ in-plane bending ca. 1450 cm^{-1} (iv) C –H out of plane bending due to mono –substituted benzene derivatives at 740 cm^{-1}(v)presence of C –O stretching ca. 1700 cm^{-1}.

The presence of the above characteristic absorptions confirms the likely presence of aromatic carbonyl compounds, phenols or alcohols.

Separation of the oil into Heptane, Toluene, Chloroform, Ethanol, Methanol and residue fractions.

The soxhlet solvent extraction method as described in the experimental section was used and it has proved to be a fairly simple, rapid and reproducible method capable of separating the oils into glasses according to chemical functionality.

The heptane and toluene fractions are mobile liquid, the chloroform fraction is very viscous liquid, the ethanol, methanol and residue fractions are solid in nature. Infrared spectroscopic showed that the predominant bond in most of the fractions are those due to hydroxyl stretching, carbonyl stretching and those characteristic of the aromatic ring.

A definite assignment for the carbonyl absorption is difficult because a number of oxygen containing compounds including aldehydes , ketones ,acids and esters absorb in the region (18). Analytical results for these runs are shown in tables 7a,7b and 8.

The chloroform, ethanol and methanol extracts account for about 80% of the product oil. The residue fraction is believed to be resinous in nature and this

fraction accounts for about 5% while the heptane and toluene fractions account for about 15% of the product oil.

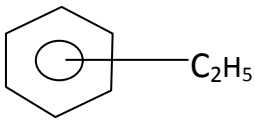
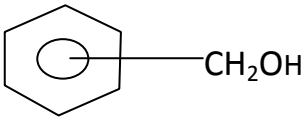
The heptane and toluene fractions contain aromatic hydrocarbons including some oxygenated compounds. Majority of these compounds are tetralin derivatives following, tentative identification by gc-ms analysis.

There is a considerable overlap between the heptane and toluene fractions. Table 10 lists the compounds found in these fractions identified by gc-ms analysis.

The chloroform, methanol and ethanol extracts are involatile and highly polar in nature, hence these fractions could not be analyzed on the gas chromatography. The phenolic nature of these fractions is evidenced by their solubility in aqueous caustic and the characteristic absorption found in the infrared spectra of these fractions. An attempt was made to separate the chloroform extract on the gas chromatograph. The compounds identified by gc-ms analysis are to be found in table 11. The aromatic moiety has been identified in this fraction and other compounds identified include monocyclic phenols with some aliphatic, naphthenic and aromatic substituent in addition to the hydroxyl group on the parent aromatic ring. Analysis also indicated the presence of poly phenols.

Separation of the highly polar and involatile fractions was however, achieved on the high performance liquid chromatograph using the reversed phase mode. Various wave lengths were tried and the oil gave the maximum absorbance at 225nm in line with with the literature value of 225nm maximum absorbance for phenolics.

Table 10

Compound type	Mol. Weight
	106
	108

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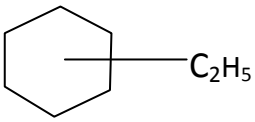

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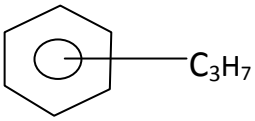

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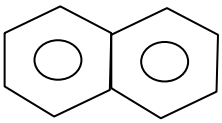

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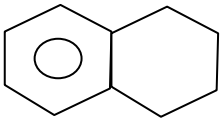

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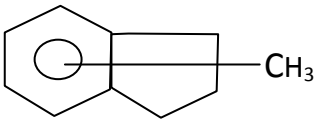

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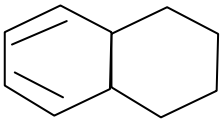

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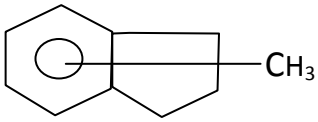

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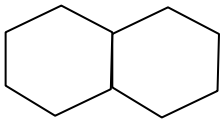

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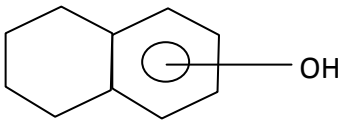

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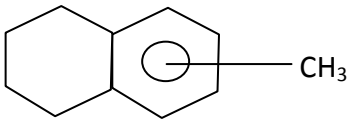

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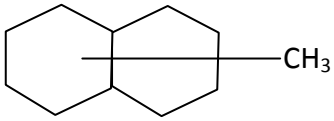

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Table 11

Compound type	Mol. Weight

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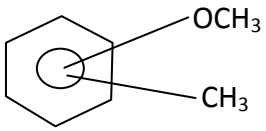

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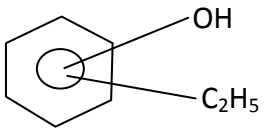

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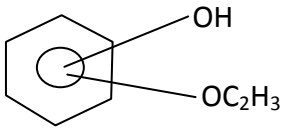

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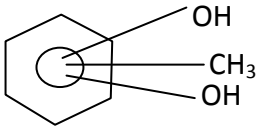

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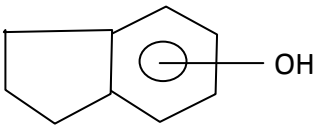

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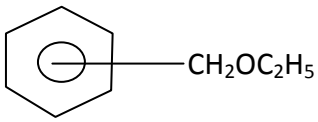

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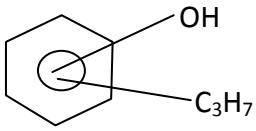

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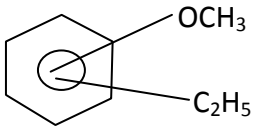

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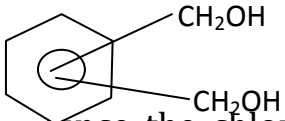

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Since the chloroform, ethanol and methanol extracts are phenolic in nature and they account for the main bulk of the product oil, the reversed phase mode was used isocratically at maximum of 225nm.

The detector is absorbance specific and to assure that the response factor is exactly the same for each component on the chromatograph would give size to a large

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error. Secondly, the linear range of the ultra violet detector in small and is the prerequisite for preparative separation is a good analytical separation of samples that falls within the linear range,loading of sample per gram of absorbent woud be small.

Therefore the components on the chromatograph would not be enough for mass spectral analysis. Moreover the mass spectra analysis would be difficult to interpret due to the interference from the solvent present in the sample. Therefore it would be important to get rid of all the solvent present in the sample before subjecting the sample to mass spectral analysis in order to avoid the interferences.

SUMMARY AND CONCLUSION

The thermal and catalytic fragmentation of Kraft lignin to oil and chemicals could Also be complicated by its rather appreciable content of oxygen. The phenyl – oxygen bond cleavage can be accomplished easily at 250 -375°c using hydro processing catalyst under a partial pressure of H_2.

Hydroprocessing of lignin to aromatics or monohydroxyl phenols would involve hydro-deoxygenation of methoxyl and hydroxyl substituted aromatics[19] . The ideal lignin hydrogenation catalyst should (i) not be deactivated by sulphur, (ii) be cheap enough to be expendable and (iii) active enough to give a high liquefaction yield.

Very little amount of gases was produced when compared to the liquid product which is a distinct advantage because liquids could be easily stored, handled and transported.

The char from the conversion may be produced theoretically by direct thermal degradation of the product oil involving dehydration, decarboxylation and homolytic cleavage of the substituents on the carbon skeleton. The char could be used for land filling, filler for plastics or it could be upgraded to provide a rich

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source of activated carbon. In any case char or charcoal is far different from pure carbon compounds such as graphite.

The product oil derived from Kraft lignin tend to be unlike petroleum derived oils in that the quality of hydrocarbon is rather low. They contain a much higher percentage of oxygen than petroleum based oils.
The properties of these petroleum based oils are often significantly different from those lignin derived oils.

Over 70% of the product oil is composed of phenolic materials. Hence this oil could make considerable inroad into the petrochemical industry as a chemical feedstock since 95% of all synthetic polymers are derived from only 3 raw materials: ethylene, butadiene and phenol.

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However, the production of phenols from Kraft lignin is not economically competitive with production from coal and petroleum. Considerable improvements have been made so that capital cost could be lowered considerably but the process has not been able to show a profitable picture. A number of reasons contributing to this lack of profitability include: (i) the monophenol product could not be obtained in as high yield as originally estimated because the catalysts have not been able to hydrogenate the aromatic nuclei which explain the reason for the production of relatively small total number of separable simple compounds. Allan et al (20) identified over thirty different phenols from lignin pyrolysis but unfortunately no single phenol dominates and various workers have revealed that the reactions of lignin aromatic methoxy groups contributes to this complexity. (ii)Depolymerization, dealkylation and eventually demethoxylation of lignin macromolecule would be necessary for converting it into valuable low molecular weight phenolic products. The destruction of such a three dimensional network would require rather drastic but carefully controlled treatments for penetration of

the structure and breakdown of the chemical linkage and specifically, the avoidance of secondary reaction providing repolymerization or condensation of the products. (iii) In the past years, monophenol prices have steadily declined so that potential returns from the process has steadily decreased.

Kraft lignin oil contains appreciable quantities of phenolic compounds and phenols seem to be present to some degree in biomass oils regardless of the source. Therefore, the problems associated with using oils for fuel probably could not be achieved by selection of biomass type.

These phenolics are quite acidic and corrosivity is a problem that should be controlled if Kraft lignin derived oils are to win wide acceptance

High viscosity which is due to the polymerization low molecular weight products is another problem that is aggravated by the higher percentage of phenolics. However, it has been found that the viscosity of the product oils can be varied by changing the reaction condition (10,11).

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In conclusion, Kraft lignin could be burned to power the mills, it has wider applications in materials application and it is also possible to substitute oil produced by liquefying Kraft lignin for petroleum based oil both as a chemical feedstock and as a fuel. This could be a panacea for the social and economic problems arising from waste disposal. The objective of this study has been realized and the economic attractiveness of the study is principally a function of the value of the raw materials, solvent, catalysts, the product oils, cost of reductants, high cost of high pressure equipment, gas purification costs to remove CO, CO_2, H_2S and in some cases, recovering excess hydrogen for recycling. Commercialization of the thermochemical technologies for the production of liquid fuels and chemical feed stocks will be based primarily on these economic considerations.

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REFERENCES

1. Brauns, F.E, The Chemistry of ligmen, Academy Press, N.Y, 1952
2. Pearl, I.A., The Chemistry of ligmen, Edward Arnold Ltd., 1967
3. Sorkaren, K.V, and Ludwig, C.H., Ligmus, Wiley – Inter Science, N.Y. 1971
4. Roberts V.M, Stein V, Reiner T, Lemonidou A, Lix, and Lercher JA, towards quantitative catalytic ligmen depolymeization, Chem. Eur. J. 2011; 17:5939 – 5948
5. Behrend. f., Neubauer Y, Oervermann M, Wilmes B, Zobal N, Direct liquefaction of Bioman, Chemical Engineering and Technology, Vol.31, Issue 5, 667 – 677, 2008
6. Veski R, Vetkov N, Trends in Burman thermochemical liquefaction : Global experience and recent studies in Estonia, Estruon Academy of Sciences: Chemistry, 2005.
7. Altgelt, K.H et al., Chromatography in Petroleum Analysis .
8. Vuori A and J.B – Son Brendenberg, Liquefaction of Kraft Lignin: 1 primary reactions under mild thermolysis conditions, Holzforschung, Vol.42, issue 2, 1988.

9. Vuori A and J.B – Son Brendenberg, Lignin model compounds, Holzforschung, Vol.38, issue 3,pp 133-140, 1984.
10. Soile O.O.B and Owoyokun T.O, Oil production from Kraft Lignin via Thermochemical Liquefaction using 3%Ru/Aly(SiO4)x, International Journal of Biomass Renewables , Vol.3 Issue 2, 2014.
11. O.O.B., Effect of varying physical Parameters on the products of the Thermo chemical liquefaction of Kraft lignin using 3%Ru/Aly(SiO4)x catalyst, International Journal of Scientific and Engineering Research Vol 5. Issue 10, 2014.
12. Brenner ,N.,Caller ,J.E.,AND Weiss ,M.D., (Eds) 'Gas Chromatography' ,3rd International Symposium,Academy Pres (1962).
13. Institute of Petroleum Standard method IP143-78 Farcasin, M., Fuel, 56, p9, 1977
14. Farcasiu, M., Fuel, 56, p9, 1977
15. Raimo Alen, Thermochemical conversion of some simple ligmen model compounds in liquid phase, Bioresource Technology, Vol.35, Issue, 1991, 103 – 106.
16. Shoolery , J.N et al ,Analytical Chemistry ,48.pp1458 ,1976.
17. Mima, M.J., In Analytical methods for coal and coal products, Karr C, Jr (Ed) ,Chapter 19, Academy Press N.Y 1978
18. Vogel ,A.,Textbook of Practical Organic Chemistry,3rd Edition.
19. Bethany, J., the infrared spectra of complex organic molecules, John Wiley and Sons, Inc., N.Y.1966.
20. Hurff, J.S ., Ind. Eng. Chem. Fundamental, 22(4), p426 ,1983.

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