

Producing Oil from Black Liquor

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Abstract

An experimental investigation was made of the hydrogenation of kraft black liquor at 350°C with CO gas and sodium or borax as catalysts. It was found that up to 65% of the fuel value of the black liquor could be converted to oil and char. The method may be useful as a means of reducing the load on a recovery boiler and simultaneously displacing fossil fuel from a lime kiln.

Introduction

There is an obvious attraction in being able to convert lignin and other organics in black liquor from pulping processes to form a fossil fuel replacement. Most previous work in attempting to form liquid fuels from forest products had concentrated on cellulose, and in particular in converting it into ethanol. Such an approach is obviously not particularly attractive in terms of best use of the organic material, as the cellulose is required for paper production. It still leaves a situation where the lignin can only be used as a fuel in rather specialised furnaces or for the production of minor quantities of specialised lignin derived chemicals. Supercritical extraction has also been studied as a means of separating lignin from cellulose but this approach does not give the lignin in a particularly useful form.

In other fields considerable work is reported in the literature on the conversion of lignin-derived materials (usually in the form of brown coal) to liquid fuels. Some literature contains work on hydrogenation of black liquor to form a fuel, but in these cases the black liquor has usually been used as a model compound. Other work on forming liquid and solid fuels from black liquor is presented in the St. Regis Hydrolysis process^{1,2} and the Wet Pyrolysis process^{3,4}. Both of these processes were attempts to replace the conventional chemical recovery furnace by a process in which the entire organic content of the black liquor was converted into oil, gas and char leaving a residual aqueous phase containing the inorganic chemicals. However, these processes also formed considerable quantities of formate, and, more importantly, acetate. These materials were resistant to further chemical change and accumulated in the aqueous phase. The same problem was also found with wet air

oxidation: the pyrolysis process could not be used as a stand alone method and some form of combustion process was required as a side stream to control the quantities of acetate⁵.

The work described in this paper was based on work originally done on the hydrogenation and liquefaction of Victorian brown coal. It had been found, as will be discussed below, that using carbon monoxide and the water gas shift reaction resulted in far more effective hydrogenation than by the use of hydrogen itself⁶. The original purpose of the experiments was to determine whether conditions could be found under which hydrogenation could be substantially completed before the water gas shift reaction reached equilibrium. The results of this kinetic work will be presented elsewhere.

On reviewing the results of this preliminary work it became apparent that the system could also have applications in the pulp and paper industry as a means of reducing the load on the recovery boiler and thus de-bottlenecking a plant. It should be noted therefore, that because the experiments were not originally directed towards the chemical recovery process, there was only limited elemental analysis of the oil and char produced in the process. Also, the distribution of sodium and sulphur between the various products of the process was not measured quantitatively. However, as will be discussed below, indirect evidence is that most of the sodium and sulphur remain in the aqueous phase.

Therefore, this paper is not presented as offering a fully developed chemical scheme but to provide information on a possible approach that others may wish to take further.

Background - Previous work on brown coal liquefaction

Both black liquor and brown coal have a common origin in lignin. It was therefore considered that previous work done in the Department of Chemical Engineering at the University of Melbourne on the liquefaction of Victorian brown coal would be a useful starting point in attempting to hydrogenate the lignin in black liquor. The process is based on using the liquid phase water gas shift reaction as the source of hydrogen.

Hodges⁷ found that the alkali metals were effective water gas shift reaction catalysts in the liquid phase hydrogenation of Victorian brown coal. He found that oil yields increased with atomic mass, as shown in Table I, and hence hydrogen production was not the limiting factor. He also noted that thermolysis of coal was required before significant oil production could occur.

Kinetic studies showed that a liquid phase reaction was occurring and the formation of an intermediate product via the water gas shift reaction was an integral part of the process. It was strongly suggested that formate was the ultimate hydrogen source and sodium formate was particularly effective in producing liquefaction. Various experiments in which carbon monoxide was added at different times after the reactants had been brought to temperature (about 350°C) showed that although the water gas shift reaction would always occur, liquefaction mainly occurred during the first 20 minutes after reaching 350°C. This process contrasts with those using molecular hydrogen which require a “donor solvent”, special catalysts and temperatures in the region of 450°C.

Table I: Effect of alkali metals and reaction time on the %oil yield from brown coal [4]

Metal	Time @ 350°C**	
	0 min	120 min
None	-	16.4
Li ⁺	-	29.0
Na ⁺	15.6	33.1
K ⁺	17.5	39.3
Rb ⁺	17.1	40.5
HCO.ONa	-	45.1

*Tests based on 60g of dry brown coal, 0.09 mol of catalyst (as anhydrous carbonate) and 1.2 mol CO.

**It took 45 min. for the reactor to attain 350°C.

Jakab⁸ et al. and also Hodges⁷ showed that in liquefaction reactions if the temperature did not exceed 350°C methane production was very low and methanol production was moderate. McKeough and Johansson⁹ also found very low yields of hydrocarbon gases and hydrogen sulphide provided temperatures did not exceed 350°.

Experimental Design

It is apparent that the lignin molecule only pyrolyses slowly even at 350° whereas in the 45 minutes it take to heat the autoclave to this temperature the shift reaction has largely reached equilibrium¹⁰. In order to try and match up the reaction rates two alternatives are possible. Either delay the onset of the shift reaction by not adding the CO until the reactants have reached 350°C or attempt

to speed up the lignin pyrolysis reaction. Two methods have been suggested in the literature to catalyse lignin decomposition. One is to use Zn⁺⁺ in the solution¹¹. This is not possible in the present case as the environment is mildly alkaline. The second method is to use borax (sodium tetraborate decahydrate¹²) and this method was used here.

Table II shows the scheme of planned tests. Sodium was used throughout as the shift catalyst. Although not the best catalyst (Table I) it is nonetheless effective, cheap, and already present in the black liquor. To ensure that the active hydrogen component was not limiting, extra sodium added for all tests. Tests were mainly conducted in pairs for direct comparison with the effect of borax. With these pairs, two sets of tests were done to check the amount of pyrolysis with time and temperature. Firstly, during the 45 minute heat up period: CO was either added initially or when 350°C was reached and in both cases quenching was started immediately. Secondly, the black liquor was held at 350°C for 20 minutes both with CO present during the whole of the heating period and then with CO added after the 20 minutes of pyrolysis. Then quenching was again started immediately.

Table II: Experimental design (tests are numbered chronologically)

Time @ 350°C (min.) ⁽¹⁾	0 ⁽²⁾		20		
		Borax		Borax	
Catalyst	-	Borax	-	Borax	
No CO addition	-	13	11	12	
Temp. at which CO added (°C)	15	9	10	7	8
	350	3, 3A	4	5	6
		-	-	14 ³	-
		- 15 ⁴	-	-	-

1. Reactor takes 45 min. to reach 350°C.
2. Reactor takes 3.5 min. to be cooled from 350°C to 200°C.
3. After CO addition, reactants held at 350°C for further 20 minutes.
4. Addition of anthraquinone (0.03 g) and glucose 0.15g).

Two further special tests were planned. First, without borax addition, the black liquor was pyrolysed for 20 minutes at 350°C, then CO was added and the temperature held for another 20 minutes (test 14).

Finally (test 15) a “donor solvent” type of test was performed in which anthraquinone and glucose (as reductant) were added to the black liquor. The CO was added at 350°C and the reactants again quenched immediately.

Since the objective of this work was to look at the feasibility of producing a value added product, only the specific energies of the products of these tests were measured. No attempt was made at a detailed chemical analysis such as O, N or S contents.

Experimental

The experiments were undertaken in a standard agitated 1L autoclave (manufactured by Autoclave Engineers). The autoclave was been modified by the addition of an Inconel liner and baffles to improve mixing effects. Cold model studies showed that gas locking of the turbine agitator was not expected. A second identical autoclave was pressurised with CO via a Haskell booster to 32 MPa. Both autoclaves had safety valves set to lift at 35.2 MPa. At 350°C the vapour pressure of water is 16.5MPa; the value for the reactants was found to be 16.1 MPa. When CO was required for the reaction the isolation valve between the two autoclaves was opened and within seconds the pressure equalised at approximately 25 MPa. This represented a transfer of some 3 mol of CO. The black liquor was derived from batch kraft eucalyptus pulping. The charge was diluted to give 15.8% black liquor solids in 188.3 g H₂O (i.e.: 100 ml black liquor solution + 100 ml H₂O; higher concentration would have resulted in the charge drying out when raised to the operating temperature). When required 10g borax was added and additional sodium was added as sodium carbonate (10g anhydrous). As required, CO was either added initially (after purging the autoclave of air) to 8 MPa (1.8 mol) which could give an operating pressure at 350°C of up to 32 MPa, or when the temperature had reached 350°C as explained above. The reaction pressure was typically 25 to 32 MPa depending on the precised reaction conditions. Under reaction conditions the solubility of CO in solution was estimated to be 0.1 mol fraction¹³.

At the end of each test the product was removed and the reactor internals scrapped clean of deposit. The total product was acidified to pH3 with hydrochloric acid, or in some samples sulphuric acid was used if the aqueous phase was to be dried out. The acidified product was passed through a 1.2 micron Millipore filter. The solids retained on the filter were extracted until a colourless reflux solution was formed in a Soxhlet apparatus using 1,1,1, tri-chloro ethane. The extracted solids constituted the char fraction. The filtrate from the Millipore filter was extracted in the separation funnel with 1.1.1. tri-chloro ethane by multiple batch extractions. On

evaporation to dryness, the residue was always less than 0.01g and was added to the soxhlet extract. The combined extract residues formed the “oil” product.

Results

The solid residue from the dried out black liquor was found to have a specific energy of 12.8 kJ/g and left a 44.5% ash residue. Hence, the 15.8 g used in each test had an energy value of 202.2 kJ. However, when 15.8g of black liquor were acid washed it yielded 5.23 g of char of energy value 129.2 kJ (no ash residue) and 0.10 g of oil was extracted of energy value 2.7 kJ. The total energy recovery was therefore 131.9 kJ. Since the acid washed material was a clean ash free material it was considered to be a better basis from which to view the results than the original dried black liquor.

The results are presented in Tables III, IV and V in the same format as Table II. The mean specific energy of the 14 chars produced was 28.1 kJ/g (standard deviation ± 6.2%). By comparison, graphite has a specific energy of 32.8 kJ/g and for a long chain paraffinic hydrocarbon the value is 46.7 kJ/g.

Table III: Char yield (g\kJ) from 15.80 g black liquor solids

Time @ 350°C (min)		0		20	
Catalyst		-	Borax	-	Borax
No CO addition		-	4.94\ 97.8	3.15\ 95.1	2.87\ 87.0
Temp. at which CO added (°C)	15	1.98\ 55.4	1.50\ 36.9	0.71\ 18.5	1.32\ 34.7
	350	1.24\ 32.7	2.23\ 64.0	1.99\ 58.9	2.81\ 86.3
		1.55\ 46.8			
		-	-		
	1.59\ 49.3	-	-	-	

*Test 13 gave a 5.8% ash residue on specific energy determination.

Table IV: Oil yield (g/kJ) from 15.80g black liquor solids

Time @ 350°C (min)		0		20	
Catalyst		-	Borax	-	Borax
No CO addition		-	0.46\ 13.1	0.25\ 8.4	1.33\ 45.0
Temp. at which CO added (°C)	15	2.62\ 82.8	2.59\ 75.6	1.50\ 48.0	3.09/ 93.3
	350	1.14\ 39.8	1.55\ 48.1	1.52\ 52.9	1.39\ 48.7
		1.28\ 43.0			
	-	-	0.47\ 15.0	-	
	2.18\ 72.2	-	-	-	

Table V: Energy recover (char & oil) as % of acid washed black liquor

Time @ 350°C (min)		0		20	
Catalyst		-	Borax	-	Borax
No CO addition		-	89.1	78.5	100.1
Temp. at which CO added (°C)	15	104.8	85.3	50.4	97.0
	350	55.0	85.0	84.8	102.4
		68.1			
	-	-	55.1	-	
	92.1	-	-	-	

As noted above, the oil and char were not analysed for sodium and sulphur content. However, chemically, it would not be expected that large quantities of sodium and sulphur would report to these phases and none of the gas, the oil or the char was odorous as would be expected if it contained considerable quantities of reduced sulphur. Nor was there the evidence of significant quantities of sulphur dioxide or ash produced when the char and oil

were burnt in the bomb calorimeter. However, further experiments would be required to confirm the ultimate department of the sodium and sulphur.

Discussion

The results were disappointing in that the original concept of complete hydrogenation to a decantable liquid oil was not realised. Also, judging by test 3 and 3A, reproducibility was worse than expected. However, they do show that (tests 6, 9 and 12) a richer fuel than that obtained from straight acid washed black liquor could be produced, with up to 68% of the original fuel value of the black liquor present in the oil and char product. The specific energy of the oils produced was some 14 kJ/g less than that for paraffin hydrocarbons and this suggest the oils had a significant oxygen content.

In straight pyrolysis (tests 11, 12 and 13) the presence of borax does appear to promote break-up of the liquor molecule and give a modest oil yield. When CO is used (test 7, 8, 9 and 10) the best oil yields were produced when it was present during the heat up period and in the presence of borax. The best result of all (test 8) was achieved by continuing the reaction for 20 minutes even though the shift reaction would have been essentially complete. However, this continued heating did not produce good oil yields (tests 5 and 6) if the CO was introduced at 350°C (in order to give the highest possible concentration of active intermediate contacting the now pyrolysed lignin).

This was especially the case (test 14) when the CO was introduced after the black liquor had already been pyrolysed for 20 minutes. A possible explanation for this is that, due to the short half-life of the intermediate, it must be produced in close proximity to the pyrolysis site for efficient use. This requires the sodium ions to be close to the lignin molecule which in turn requires the carboxylic radicals to remain intact. Unfortunately, at 350°C the carboxylic radicals are rapidly destroyed. A better oil yield might therefore have been obtained by using borax but operating at a lower temperature, say 300°C (this would also have practical benefits for equipment to be used). The use of anthraquinone as a hydrogen donor gave a promising result and could be usefully investigated further.

From the point of view of mill operation, the pyrolysis process in the presence of the shift reaction produces four separate products:

- A gas phase containing carbon dioxide and hydrogen, some of which may be recycled to the pyrolysis process, and the remainder used as fuel in the lime kiln or the recovery boiler.

- An aqueous phase which would contain most of the sulphur and sodium for the original black liquor, plus 30 to 50% of the fuel value. This liquor would be returned to the weak black liquor, evaporated, and then fed to the recovery boiler along with the bulk of the black liquor.
- Char, which can be used as a fuel.
- Oil, which is the preferred product and which can also be used as a fuel.

The oil and char will tend to be formed as a stable but easily separable aqueous suspension. The char and oil can be separated by various means. However, for most applications, it would probably be preferable to maintain them as a char in oil slurry and feed this as fuel to the lime kiln or to some other combustion device. In this way, not only is the recovery boiler load decreased, but the quantity of fossil fuel required for the lime kiln is also substantially decreased as shown in table VI. About 10 to 15% of the fuel value of the original black liquor would be required to fuel the lime kiln thus representing an equivalent reduction in the duty on the recovery boiler. Some more of the oil and/or char may also be used in the generation of carbon monoxide to run the hydrogenation process.

If required, the thermal load on the recovery boiler could be further reduced by processing a larger proportion of the black liquor. The oil and char so produced could be further refined, or be fed to a power boiler. Obviously, there are limits here depending on both of the amount of sodium and sulphur contained in the oil and char, and the tolerance towards these elements of the power boiler (for example, more sulphur can be accepted if a boiler with flue – gas desulphurisation is employed, such as a fluidised bed with limestone addition). There will also obviously be a limit determined by the ability of the

recovery boiler to operate with an increased inorganics to organics ration.

Table VI Example of possible savings

Typically:	ca.1 t Black liquor organics produced with 1 t pulp. Specific energy of Black liquor organics = 19 MJ/kg. Specific energy of Black liquor solids = 12.8 MJ/kg. Lime burning requires 5.7 MJ/kg kiln product. ca 0.25 t lime required for causticising per t pulp.
Therefore:	Fuel requirement for kiln is ca 1430 MJ/t pulp.
So -	about 11% of Black liquor fuel value goes to oil and char to supply kiln and for CO generation.

Conclusion

Although the original objective was not achieved it has been shown that upgrading black liquor as a fuel is possible and the shift reaction is beneficial to this process.

The overall effect remains one of an ability to simultaneously reduce the thermal load on the recovery boiler and at the same time to replace fossil fuels with fuels generated in the mill from the lignin component of the woodchips.

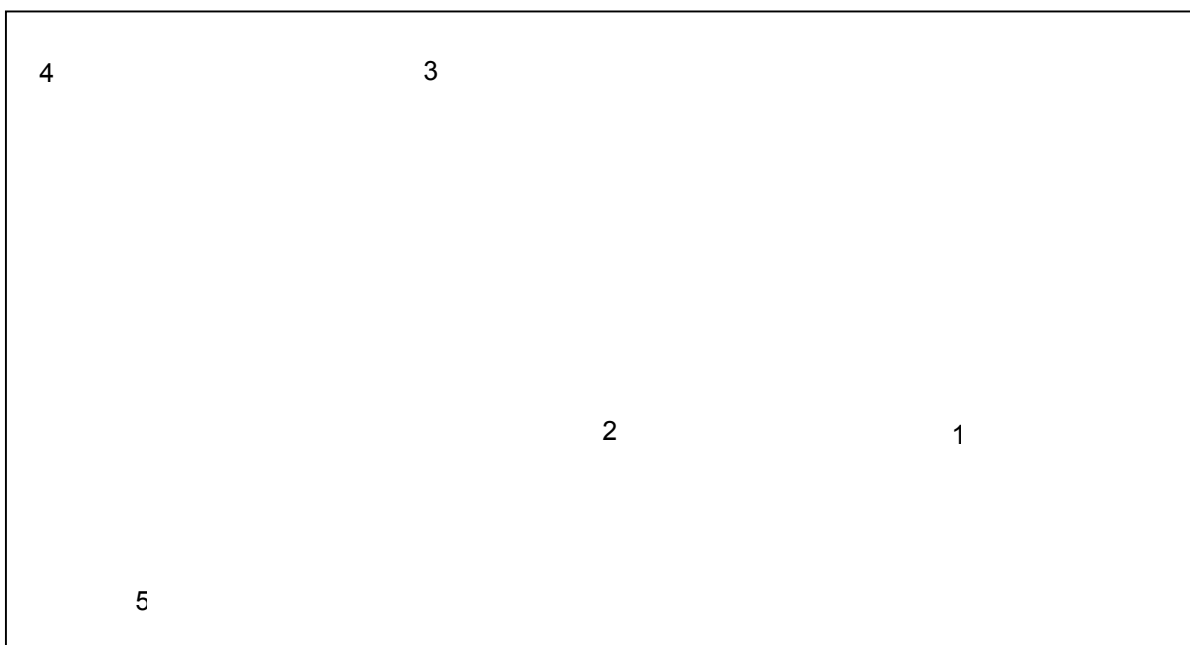


Figure 1. Diagrammatic view of apparatus (1 Reactor, 2 CO Reservoir, 3 Haskel booster, 4 Compressed air, 5 CO bottle).

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