CONTINUOUS HYDROLIQUEFACTION TESTS OF AUSTRALIAN BROWN COAL

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INTRODUCTION

The Australian state of Victoria possesses huge proven reserves (66.7×10^9 tonnes) of brown coal which have been shown (1-3) to be highly suitable for hydrogenation to liquid fuels. Previous ACIRL (3) batch autoclave tests on Victorian brown coal gave toluene-soluble liquid yields of 61% when hydrogenated in tetralin at 400°C for 4 hours at hydrogen pressure of around 21 MPa. Moreover, high yields of oil have been reported (4) for the hydrogenation of German brown coals (similar to the Victorian variety) in large-scale continuous operations.

Hydroliquefaction tests on a Victorian brown coal in ACIRL's 1 kg/hr continuous reactor unit are reported here. The unit and supporting equipment have been described earlier (5) with reference to black coal hydrogenation tests.

CONTINUOUS REACTOR OPERATIONS

The brown coal sample was from a steam-dried batch of run-of-mine brown coal then exposed to ambient room conditions for several hours. The coal was then crushed and screened to pass .075 mm and stored in polyethylene bags until required. Equilibrated moisture contents determined by the Dean and Stark (boiling toluene) method were in the range 11-16%.

The conditions under which these tests were run were -

Slurry solvent/coal ratio	1.68 - 2.0 : 1
Slurry feed rate	0.7 - 1.0 kg/hr
Hydrogen feed rate	88 - 92 g/h
Catalyst % Coal	0 - 4.3
Temperatures:	
Preheater	25 - 450 C
Reactor	25 - 430 C
Preheater tube dimensions	6 - 25 m long x 6 mm I.D. x 9.5mm O.D.
Reactor volume	3.5 L

Table 1 gives further run details.
The reactor internal configuration is shown in the figure. The reactor has been divided into three stirred compartments in an effort to increase the number of CSTR stages with minimal interstage backmixing, and thus to approach plug flow which is known to be more effective for a given reactor volume.

OPERABILITY

Feed slurry solvent/coal ratios were limited to above 1.68 : 1 as thicker slurries could not be pumped satisfactorily. At larger scales of operation it is likely that thicker slurries could more readily be handled. Accordingly, the data obtained at this small scale may be affected by the low feed slurry coal concentrations that could be achieved.

Product slurry let-down valves operating with pressure drops of up to 21 MPa down to atmospheric have survived longer (over 200 hours) in brown coal service than in black coal runs (50-100 hours). This is most likely the result of lower ash contents and lower percentages of hard macerals in brown coal.

Preheater tube blockages have been encountered in every run with brown coal. We observed that high temperatures tended to accelerate deposition of mineral matter and coke on the preheater wall. Deposition of solid coke-salt materials in preheaters also appears to be a problem for other workers in brown coal and lignite hydrogenation. High levels of calcium have been qualitatively observed in some of our preheater solids. However the original deposit that eventually caused a blockage could not always be found because preheater contents tended to coke along the whole length when flow stopped. The original high-calcium deposit was then only locatable by laboriously cutting the whole preheater into many sections and examining each one individually.

RESULTS

Observed mass balances and oil yields are presented in Tables 2 and 3. Yield data corrected to 100% recovery for operationally stable runs 33, 44 and 45 are presented in Table 4. Overall recoveries for these runs were 95- 96%.

Because of the small scale of operations perfect mass balances were very difficult to achieve. Overall mass balances varied from 82% to 97%, the poorer mass balances being partly attributable to operational problems such as leaks, necessarily hasty remedial action to clear blockages in the feed slurry circulating system, and losses when discharging material in process in order to replace a blocked preheater. Distillation mass balances (i.e. recovery of water, light oil, middle and vacuum distillates and distillation residue) were 95 - 98% of product slurry fed to the distillation equipment. Observed oil yields were corrected by assuming perfect recovery. Thus, observed oil yields in the range 31 - 44% for overall 95 - 96% recoveries are estimated to be in the range 42 - 55% assuming 100% recovary. We believe that the downside error is unlikely to be greater than 5%, that is the above oil yield range is unlikely to be less than 26 - 39%.

Observed distillate yields for runs with poor overall recoveries are unfortunately suspect. However, some conclusions can be drawn with reasonable certainty, namely:

(a) Distillate oil yields of up to 55% can be obtained from this coal at conditions attainable in this bench unit.

(b) Oil yields were higher when reactants flowed through both preheater and reactor (both at above 400°C) than through either alone. Some negative oil yields were observed probably as the result of degradation of solvent in the hot preheater.

(c) Solids building up in the preheater tended to reduce liquid yields probably due to decreasing reaction volume.

(d) Preheater deposits tended to form more rapidly at higher temperatures.

(e) Added red mud and sulfur improved liquid yields slightly. Further verification of this effect is under way.

PRODUCT CHARACTERISTICS

Light oils (IBP - 200°C) were found to contain 19-37% paraffins, 19-27% naftenes, 26-50% aromatic hydrocarbons, and 9-14% oxygenated compounds, mainly phenols and ketones. This would suggest that substantial extraction and/or catalytic hydrotreatment would be required to produce a suitable feedstock for gasoline. By comparison light oils derived from black coals generally contain about half as much oxygenated compounds.

The heavier oils from which aliquots are used as recycle oil, contained substantial concentrations of heteroatoms of which phenolic hydroxyl groups accounted for 70-90% of the oxygen present. The concentration of saturated hydrocarbons increased up to 10% with succeeding recycle passes while aromatics and simple polar compounds remained approximately constant. Branched hydrocarbons were present in only very small amounts. After about 400 hours total operation, indications were that 30-40% of the original starting solvent components remained. In other words, the original starting solvent (mildly hydrogenated creosote) is fairly stable at these hydrogenation conditions and thus it merely becomes diluted with every succeeding recycle pass.

CONCLUSION

It is important to recognise that these data were generated on a small bench unit and are indicative of trends and likely ranges of oil yields. These runs have provided valuable experience enabling us to better plan future improvements to improve mass balances and yields. However, we believe that at this small scale the best recoveries achievable are 98% on feed slurry, that is 95-96% on feed coal.

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TABLE 1.

Run Conditions

Runs	Duration h	Brown Coal feed kg	Starting Solvent	Solvent/ Coal Ratio	Catalyst % coal
33	98	25	100 % MHC	1.68 : 1	4.3
34-36	311	85	100% MHC then RS from previous runs	1.75 - 2.0 : 1	0 - 1.2
44A, B	100	30	49% MHC 51% RS from previous runs	1.80 : 1	4.0
45	106	35	100% RS from Run 44	1.80 : 1	4.0

MHC = mildly hydrogenated creosote
RS = recycle solvent
Catalyst = 75% red mud + 25% elemental sulfur.

TABLE 2.

Unit Configuration and Preheater Behaviour

Runs	Preheater			Reactor	
	Temperature C	Status	Time to block, h	Temperature C	Status
33	450	In	71	425	In
34A	450	In	-	-	Out
34B	450	In	89	425	In
35A	450	In	53	425	In
35B	450	In	26	-	Out
36A	450	In	-	-	Out
36B	450	In	50	370	In
36C	-	Out	-	425	In
44A	435	In	59	430	In
44B	410	In	-	430	In
45	410	In	86*	430	In

* Blockage cleared by imposed excess pressure drop. All other blocked preheaters could not be cleared and were therefore replaced.

TABLE 3.

Mass Balances and Yields

Run	Mass Balance Closure on Total Feeds (%)			Observed Distillate Yield % d.a.f. Coal
	Continuous Reactor	Distillation	Overall	
33	100.1	94.7	95	44
34A	85	97.9	83	-16
34B	84	97.6	82	- 5
35A	89	96.5	86	- 2
35B	95	98.7	94	3
36A	101.4	98.6	97	-11
36B	98.0	97.2	95	- 7
36C	89	98.2	87	11
44A	97.4	97.4	95	31
44B	97.6	97.4	95	38
45	98.3	97.8	96	32

TABLE 4.

Yields Corrected to 100% Recovery

Run	33	44A	44B	45
IN				
Coal (d.a.f.)	100	100	100	100
Hydrogen consumed	6	10	12	7
	106	110	112	107
OUT				
C_1 - C_4 hydrocarbons	13	17	13	11
CO, CO_2	12	17	14	15
Heterogases	2	1	1	3
Generated Water	12	13	12	15
Light Oil (IBP - 200°C)	10	13	10	10
Middle Distillate (200 - 320°C)	28	25	29	22
Vacuum Distillate (320 - 550°C)	17	7	13	10
Distillation Residue (d.a.f.)	12	17	20	21
	106	110	112	107
Net distillate Oil Yield, % d.a.f. coal	55	45	52	42

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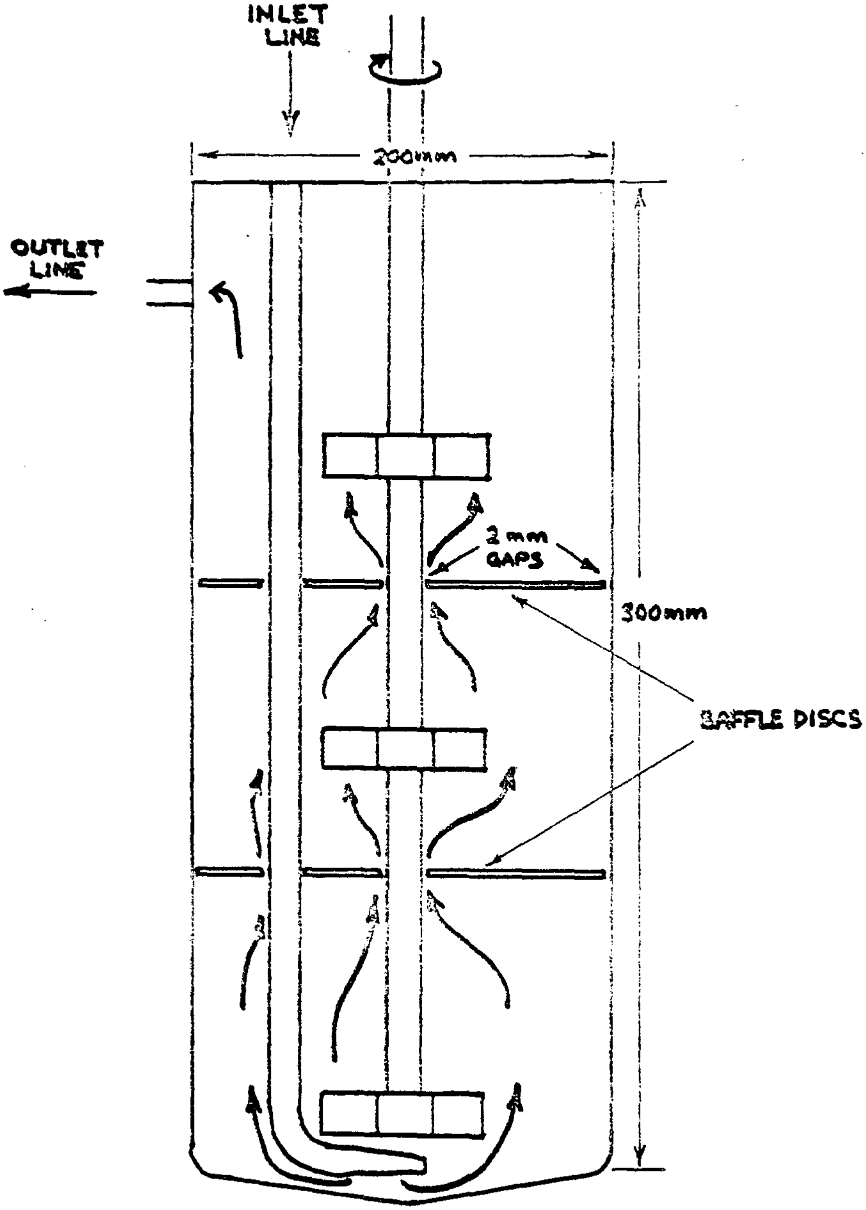

Internal Configuration of Stirred Reactor