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SUMMARY

The overall chemistry of Douglas Fir liquefaction as evidenced by Rust Engineering Company's Test Run 8 at Albany, Oregon has been examined. It is concluded that the true total yield of non-gaseous product (oil + water solubles + char) is higher than was measured -- probably as high as 52-55% of dry wood feed. Wood decomposes to give water and carbon dioxide, and carbon monoxide in the gas feed reacts with water to give carbon dioxide and hydrogen. However, there is a substantial net reaction of synthesis gas ($CO + H_2$) during the process. This indicates that the reaction CO + (wood product) = CO_2 + (reduced wood product) is important in formation of low oxygen product oil. Overall stoichiometry (approximate) is:

100 lbs wood + 0.5 Mol CO $\rightarrow$ 1.1 Mol CO_2 + 0.5 Mol H_2O + 55 lbs non-vapor product.

Consumption of synthesis gas in the process is (very approximately) 1300 SCF/bbl product. The product oil has a hydrogen/carbon atom ratio of 1.2 and is highly aromatic.

This analysis of the reaction applies specifically to the particular mode of operation used at Albany; i.e., to the so-called PERC process with a very high recycle of product oil. However, it is shown that the total yield of non-gaseous products is quite insensitive to the average analysis of the product. Thus we would expect total yields in the 50s with alternate processes -- such as the LBL water slurry process. What will be different and must be determined is the distribution among water insoluble oil, water solubles and char and the degree of reduction of oxygen content by reaction with carbon monoxide.

A discussion of mechanisms of reaction and of the contributions of cellulose, lignin etc. to the various products is left for a later report.

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INTRODUCTION

There exists considerable question about the stoichiometry of the overall reactions which occur when wood is converted to soluble oil in the presence of steam, carbon monoxide and hydrogen under pressure. Recent tests (1) at the Albany, Oregon Biomass Liquefaction site, operated by Rust Engineering under DOE contract, have yielded helpful data. Based on Test Run 8 (operated in the "PERC" mode, with a high recycle ratio of product oil to Douglas Fir wood flour), several observations can be made:

- A large proportion of the carbon monoxide feed is converted to hydrogen and carbon dioxide gas via the water gas shift reaction.
- However, there is also a considerable net usage of synthesis gas (hydrogen plus carbon monoxide) in the process.
- Large amounts of carbon dioxide are formed by decomposition of feed wood -- in addition to that made by reaction of wood with carbon monoxide.
- Very little hydrocarbon gas is made.
- Total conversion of wood to products other than char is high -- with good operation about 98%.
- In general, the product oil is suprisingly stable.

With a very high recycle (about 8:1) of total recovered liquid product and a single-pass liquid space time of about two hours at 360°C, no effect of processing on the viscosity and char content of the recycled liquid could be detected. Both viscosity and char content increased, however, when agitation became worse because of failure of the reactor stirrer.

With Rust Engineering's actual data in hand, I have made some quantitative calculations and used these as guides to estimating the overall stoichiometry.

The complex nature of wood -- Douglas Fir is roughly 41% cellulose, 26% hemicellulose, 28% lignin, 5% other organics and 0.3% ash -- makes it difficult to interpret this stoichiometry on a molecular basis. I make no attempt here. Nor is there any way of deciding whether the high ratio of recycle oil to fresh feed in the PERC runs effects the stoichiometry. Certainly there may be solvolysis of feed wood by the recycle oil, perhaps aiding reaction. Also there may be a continuing reaction of oil with synthesis gas upon recycle. Thus the stoichiometry may be somewhat different from that to be expected in a one-pass operation such as the LBL process.

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(1) Technical Progress Report, April-June 1980, Operation of Biomass Liquefaction Facility, Albany, Oregon, Rust Engineering Co., Aug. 7, 1980.

Calculations From Albany Data, Test Run 8

In the Rust Engineering Progress Report (1) for April-June 1980, material balance data are given for two data windows. Of these two, TR 8B is believed to be superior because of a failure of reactor agitation during the second period, TR 8C. However, I have attempted atom balances around both periods.

Table I shows a summary of the calculations for TR 8B, Table II for TR 8C. There are substantial differences between the two periods, and clearly neither balance is perfect. However, some conclusions can be drawn:

- o A substantial part of the CO feed reacts with water to form CO_2 and hydrogen. The two periods disagree on the amount shifted; it is very roughly half of the input CO.
- o A large amount of CO_2 is generated by wood decomposition. Again the two periods disagree; 10 to 20% of the feed carbon appears in the gas as CO_2 carrying with it 30 to 70% of the oxygen.
- o There is substantial reaction of synthesis gas with wood (CO + wood $\rightarrow CO_2$). Roughly 1/5 to 1/4 of the wood oxygen seems to be removed as CO_2 through this reaction.
- o Considerable hydrogen is removed from the wood. This must be by decomposition of wood components to give H_2O. Roughly 0.7 to 0.8 lb mol water is formed per hundred lbs wood feed. From the individual atom balances, some conclusions about the overall balances in the two periods can be drawn:
- o In 8B there is less carbon, but much more oxygen in the outputs than in the feed wood. This indicates that the true non-gaseous product (oil + char + water solubles + losses) is greater than I have assumed and that the gas yield (or the CO_2 analysis) is too high.
- o In 8C the carbon recovery is very low, but the oxygen recovery is all right. However, balancing carbon requires assuming both higher non-gaseous product and additional gas. This would again result in some excess oxygen recovery.
- o Considering the high recycle ratio in the test run and the low ratio of new oil made to recycle oil (5% per pass), the balances must be considered as good as or better than might be expected.

Test Atom Balances with Forced Closure

When we attempt to force a closure of all three major atom balnces, C, H and O, we find that the observation that at least some synthesis gas reacted demands that there be a minimum yield of non-gaseous product. With the assumptions I have made this minimum yield is 51 to 52%. Tables III and IV show forced balances at 55% yield and 52% yield respectively.

The 52% assumption results in a calculation of a very low synthesis gas utilization which is contrary to observation. With 51% yield assumption, we calculate essentially zero utilization. At 55% the following conclusions are drawn:

- o 84% of C is in non gaseous product, 16% is gas.
- o 49% of O is in CO_2 by decomposition, 20% in H_2O found by decomposition, 21% in CO_2 formed by CO reaction with wood.
- o 18% of H is in water formed by decomposition, balance in oil, water solubles or char.
- o Of 100 lbs of wood, 45 lbs goes to gas or H_2O. This includes 37.6 lbs oxygen, 1.0 lbs hydrogen and 7.4 lbs carbon.

The above observations are compatible with the average experimental observations based on Tables I and II when allowance is made for the excess oxygen recovery in test 8B.

Effects of Analysis Assumptions on Conclusions

The assumption that the overall non-gaseous product has the same analysis as that reported for recovered product oil has, of course, an influence on the forced material balance. If the assumed losses are such as to raise the average oxygen content to -way- 12%, the yield must be raised two or three percent above 55% to effect a balance. Small errors in the hydrogen analysis have very little effect on the calculated total yield. They merely require that more or less of the oxygen be lost by water formation with a compensating change in that lost by CO reduction.

In practice it seems likely that the average analysis of the char and water solubles is not sufficiently different from that of the oil recovered to affect the atom balance significantly. The "losses", however, could be oil as I have implicitly assumed, or, in the extremes, unreacted wood or carbon-rich char. If they are wood, the non-gaseous "yield" from some portion of the feed is 100% and the overall yield of non-gaseous product is higher than 55%. This is a possibility only if losses are spilled wood feed or the result of faulty feed measurement. This seems improbable.

Suppose some of the wood went to a char having the analysis, C - 93.0% H - 3.0% O - 4.0% and that all the loss of H and O (wood to char) resulted from decomposition to $H_2O + CO_2$. (cf Table V).

Once again, if we assume a 55% yield, we can force a balance. With lower assumed yields we get less than 100% carbon recovery.

The yield of non-gaseous product is, then, insensitive to the assumed product analysis or the assumed nature of unrecovered product. It is somewhat sensitive to the feed wood analysis, dropping 1.38 lbs/100 lbs feed for each 1% rise in the wood oxygen analysis.

Summary of Overall Chemistry

Douglas Fir wood is converted to oil plus small amounts of water-soluble products and char at about 52-55% wt % efficiency. Based on my approximate stoichiometric analysis, the following changes occur.

100 lbs dry wood → 0.6 Mol CO_2 (by decomposition)
+
+ 0.5 Mol CO   0.5 Mol CO_2 (by reduction)
+
0.5 Mol H_2O (by decomposition)
+ 53-55 lbs oil + char + water solubles.

Carbon monoxide used is about 200 SCF/100 lbs wood or 370 SCF (100 lbs product or ∿ 1300 SCF/bbl product.

The yield of non-gaseous product can be less than 51% (under my assumptions about analysis) only if carbon monoxide is generated by decomposition of wood or by reaction of wood or its products with water. This is contrary to observation.

TABLE I

Atom and Molecule Balances for Test Period 8B

A. Gas in and out

IN

Component	Mol %	SCF†	Mols
CO	60.1	3501	9.2
H_2	39.5	2301	6.1
N_2	0.4	24	0.1
Totals	100.0	5826	15.4

OUT (dry product gas)

Component	Mol %	SCF	Mols
CO	1.8	189	0.5
H_2	42.5	4463	11.8
N_2	1.6	168	0.4
CH_4	0.7	74	0.2
CO_2	53.4	5608	14.8 (14.6*)
Totals	100.0	10502	27.7

	NET CHANGE	CHANGE BY SHIFT	CHANGE BY CO + WOOD	CHANGE BY WOOD DECOMPOSITION
CO	- 8.7	- 5.7	- 3.0	--
CO_2	+ 14.6	+ 5.7	+ 3.0	+ 5.9
H_2	+ 5.7	+ 5.7	--	--
CO + H_2	- 3.0	--	--	--
CH_4	+ 0.2	--	--	+ 0.2
N_2	+ 0.3	--	--	--

† 379 SCF = 1 lb Mol

* Corrected for CO_2 from Na_2CO_3 catalyst.

B. Dry Wood Feed/Oil and Char Product

Dry Wood in (668 lbs)			Oil + char + H_2O Soluble out (307 lbs*)			
Atom	wt %	lb atoms	Atom	wt %	lb Atoms	Difference Atoms
C	53.2	29.59	C	83.9	21.45	8.14
H	5.6	37.11	H	8.3	25.28	11.83
O	40.5	16.91	O	7.5	1.44	15.47
N	0.13	.06	N	(0.1)	.02	.04
Others	0.57	--	Others	(0.2)	--	--
Totals	100.0	83.67	Totals	100.0		

C. Overall

ATOM	C	H	O	N
In Oil	21.45	25.28	1.44	.02
In CO_2 by decomposition	5.9	--	11.8	--
In CH-1	.2	.8	--	--
In CO_2 by reduction	--	--	3.0	--
In N_2				.6
TOTALS	27.6	26.3	16.2	.6
CF Wood Input	29.6	37.1	16.9	.1
Difference	-2.0	-10.8	-0.7	+.5
Atoms in H_2O needed to balance H-Atoms	-2.0	+ 0.0	+4.7	--
Remaining difference	--	10.8	5.4	--
Products - wood				

* Assumes oil yield = 46% (41 observed + 2% char + 3% in water products)

TABLE II

Atom and Molecule Balances for Test Period 8C

A. Gas in and Out

IN				OUT				
Component	Mol%	SCF	Mols	Component	Mol%	SCF	Mols	
CO	58.9	4473	11.8	CO	15.6	1520	4.0	
H_2	41.1	3122	8.2	H_2	42.0	4092	10.8	
N_2	0.0	--	0.0	N_2	0.8	78	.2	
Totals	100.0	7595	20.0	CH_4	0.5	49	.1	
				CO_2	41.1	4004	10.6	(10.4*)
				Totals		9743	25.7	

	Net Change	Change by Shift	Change by CO + Wood	Change by Decomposition
CO	-7.8	-2.6	-5.2	--
CO_2	+10.6	+2.6	+5.2	+2.6
H_2	+2.6	+2.6	--	--
$CO + H_2$	-5.2	--	--	--
CH_4	+0.1	--	--	+0.1
N_2	+0.2	--	--	--

* Corrected for CO_2 fro Na_2CO_3

TABLE II (continued)

B. Dry Wood Feed/Oil and Char Product

Dry Wood in (700 lbs)			Oil + Char + Oil in H_2O Out (322 lbs*)			
Atom	wt%	lb atoms	Atom	wt%	lb atoms	Difference (atoms)
C	53.2	31.01	C	83.9	22.50	8.51
H	5.6	38.89	H	8.3	26.52	12.37
O	40.5	17.72	O	7.5	1.51	16.21
N	0.13	.07	N	(0.1)	.02	.05
Others	0.57	--	Others	(0.2)	--	--
Totals	100.0	87.69				

C. Overall

ATOM	C	H	O	N
In Oil	22.5	26.5	1.5	0.4
In CO_2 by Decomposition	2.6	--	5.2	
In CH_4	0.1	0.4	--	
In CO_2 by Reduction	--	--	5.2	
In N_2	--	--	--	0.4
Totals	25.2	26.9	11.9	0.4
cf wood input	31.1	38.9	17.7	0.1
Difference	-5.9	-12.0	-5.8	+0.3
Atoms in H_2O needed to balance H-Atoms	--	(+12.0)	(+6.0)	--
Remaining difference Products - wood	-5.9	±0	+0.2	

* Assumes oil yield = 46% (41 observed + 4 char + 1 in water product)

TABLE III

CONVERSION OF DOUGLAS FIR
TO OIL

A POSSIBLE ATOM BALANCE

INPUT

Atom	Lbs.	Atoms
C	53.2	4.43
H	5.6	5.62
O	40.5	2.53
Others	9.7	
	100.0	

PRODUCT OIL ANALYSIS

C - 84.0
H - 8.5
O - 7.5

OUTPUTS (55% Yield of Oil + Char + Liquor Solubles)

(A) OIL (+ char and liquor)			(B) CO_2 by decomp		(C) H_2O by decomp.		
Atom	Lbs	Atoms	Lbs	Atoms	Lbs	Atoms	Total Lbs
C	46.20	3.85	6.97	0.58	-	-	53.2
H	4.68	4.64	-	-	0.97	0.96	5.6
O	4.12	0.26	18.56	1.16	7.68	0.48	30.4
Totls	55.0		25.53		8.90		89.2

(D) Oxygen lost by reduction - 0.63 Atom = 10.1 lbs.
Total lbs output = 55.0 + 27.24 + 9.12 + 8.6 + 0.7 = 100.0
Mols syngas used = 0.63 = 239 SCF = 434 SCF/100 lbs product
= 1500 SCF/bbl.

TABLE IV

A SECOND POSSIBLE BALANCE

Outputs (52% oil + char + liquor solubles)

	(A) OIL		(B) CO_2 by Decomp		(C) H_2O by Decomp		Total Lbs.
	Lbs	Atoms	Lbs	Atoms	Lbs	Atoms	
C	43.7	3.64	9.5	0.97			53.2
H	4.42	4.39	-	-	1.2	1.21	5.6
O	3.90	.24	25.3	1.58	9.7	0.61	38.9

Oxygen lost by reduction = 40.7 - 38.9 or 1.8 lb = 0.11 Atom
Syngas used = 0.11 Mol or 42 SCF/100 lbs wood
= 26 SCF/100 lbs product
= 265 SCF/bbl product

Note: From Rust Report oxygen lost by decomposition to CO_2 and by reduction are:

	Run 8B	Run 8C
By decomposition to CO_2	28.3	11.9
By reduction with syngas	7.2	11.9
Add: (1) - O in oil	3.4	3.4
(2) - O in H_2O lost	12.9	13.7
TOTAL	51.8	40.9
cf O in wood	40.5	40.5

TABLE V

Forced Balance - Wood to Char

Output - 55 lbs char	lbs		Totals
	Loss as H_2O	Loss as CO_2	
C - 51.2 lbs	--	23	53.5
H - 1.65 lbs	4.05	--	5.7
O - 2.2 lbs	32.4	61	40.7
			99.9