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COPROCESSING OF CANADIAN LIGNITES AND BITUMEN

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by

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ABSTRACT

Simultaneous upgrading of Canadian lignites and bitumen under various operating conditions was investigated in a continuous hydrogenation unit.

Results indicate that:

- coprocessing of lignites and vacuum bottoms is feasible and the results are comparable to those obtained from subbituminous coal using the same coprocessing medium;
- coal and pitch conversions appear to increase linearly with temperature over the range investigated;
- distillate and gas yields appear to increase linearly with increasing pitch conversion;
- hydrogen (equivalent) consumption ranges from 2 to 3 wt % of slurry feed (maf); and
- qualities of distillates are comparable to those of No. 6 fuel oil.

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INTRODUCTION

The Coal Liquefaction Section of Energy Research Laboratories (ERL) Canada Centre for Mineral and Energy Technology (CANMET) is currently engaged in a research program on coprocessing (1,2,3). This involves simultaneous processing of heavy hydrocarbon fractions such as petroleum crude oil, atmospheric tar bottoms, vacuum tar bottoms, heavy recycle oils, crude oil residues and heavy bitumen oils with coals of various ranks. In this process slurry feed containing fine coal particles is processed in a continuous flow reactor at high temperature and pressure under reducing atmosphere. The slurry medium, i.e., the heavy hydrocarbon fraction, appears to act as a hydrogen donor in the coal liquefaction reaction while being upgraded to lighter fractions (4,5).

In coprocessing the slurry medium is processed in a once-through mode and constitutes a major portion of the feedstock (6). Consequently, a coprocessing facility of given unit reactor volume can produce significantly larger quantities of products than can an ordinary direct liquefaction facility that requires solvent recycle.

The operability of coprocessing depends on temperature and pressure. Even though reaction temperature is not excessively high, if the pressure of a reducing gas in a coprocessing reactor is too low, the stabilization of reactive hydrocarbon radicals by the reducing gas becomes slower compared with the production of the radicals, resulting in regressive polymerization, or coking.

In addition, preliminary investigations at ERL showed that the operability of coprocessing was strongly dependent on the combination of slurry medium and coal.

The present study examines the coprocessing performance of Saskatchewan lignites (Coronach and Bienfait) and Cold Lake vacuum bottoms, in terms of the effects of operating temperatures and pressures on the coal and pitch conversions, hydrogen consumption, product yields, and the degree of hydrogenation and overall heteroatom removal. The results are compared with those obtained using the same slurring medium and an Alberta subbituminous C coal.

PROCESS

A schematic flow diagram of the CANMET coprocessing unit is shown in Fig. 1. A Saskatchewan lignite (Coronach or Bienfait) was pulverized and sieved. The pulverized coal was mixed with the CANMET additive and Cold Lake vacuum bottoms in the slurry feed tank. The slurry feed was pumped into the bottom of a stirred tank reactor with compressed, and preheated hydrogen or synthesis gas. The hydrogenated slurry and gases overflowed from the reactor through a stand pipe. Heavy fractions were collected in a sample receiver under high pressure and light fractions carried over with the gaseous stream were condensed and collected in a light ends collector under high pressure. Non-condensable gases were scrubbed under pressure, pressure reduced to atmospheric pressure, scrubbed again, and metered before they were vented to the atmosphere.

RESULTS AND DISCUSSION

Table 1 summarizes the properties of the feed coals and Cold Lake vacuum bottoms (solvent). For comparison the properties of an Alberta sub-bituminous C coal are also shown.

Table 2 shows the process performance at various operating conditions. The definition of coal conversion is given by:

$$\text{Coal conv. (wt \%)} = \frac{\text{THF insol. in feed} - \text{THF insol. in product}}{\text{THF insol. in feed}} \times 100$$

Similarly pitch conversion is defined by:

$$\text{Pitch conv. (wt \%)} = \frac{525^{\circ}\text{C+ fraction in feed} - 525^{\circ}\text{C+ fraction in product}}{525^{\circ}\text{C+ fraction in feed}} \times 100$$

Both yields and hydrogen consumption (wt %) are based on maf slurry feed.

Figure 2 shows the effect of reactor temperature on the coal conversion. The coal conversion appears to increase linearly with the reactor temperature at a given operating pressure and space velocity. Significant coal conversion occurs even at relatively mild conditions. The use of synthesis gas instead of hydrogen appears to have little effect on the coal conversion. The broken line in Fig. 2 shows previous results for Cold Lake vacuum bottoms

and the subbituminous coal. The difference in coal conversions between Saskatchewan lignites and the subbituminous coal is small.

Figure 3 shows the effect of temperature on the pitch conversion. The pitch conversion also appears to increase linearly with increasing reactor temperature. The slope of pitch conversion is slightly steeper than that of coal conversion; indicating a higher temperature dependence for the pitch conversion than for coal conversion. The coprocessing of Cold Lake vacuum bottoms with Saskatchewan lignites resulted in slightly lower pitch conversions than those obtained with the subbituminous coal. This indicates the sensitivity of the process to the combination of coal and slurrying medium.

Figure 4 shows gross yields vs. pitch conversion. The distillate is defined as the fraction of the product that boils below 525°C. The gases are hydrocarbon gases between C_1 and C_4 only. Both the distillate and gas yields increase linearly with higher pitch conversion. The gross yields obtained from the subbituminous coal are shown as broken lines. Saskatchewan lignites give slightly lower distillate and gas yields than the subbituminous coal. Again synthesis gas appears to have little effect. Figure 5 shows hydrogen (equivalent) consumption vs. pitch conversion. The hydrogen (equivalent) consumption accounts for the consumption of carbon monoxide in synthesis gas feed as being equivalent to the hydrogen consumption. Despite relatively large scattering the hydrogen (equivalent) consumption lies between 2 and 3 wt % of maf slurry feed. As observed with the subbituminous coal, synthesis gas runs appear to consume slightly less hydrogen (equivalent) than the hydrogen only runs. According to the subbituminous coal runs the difference diminishes at high pitch conversion and the hydrogen (equivalent) consumption approaches 3 wt %.

Figure 6 shows the heteroatom removal and hydrogen addition vs. pitch conversion. The removal and addition are expressed in relation to the elemental analysis of the slurry feed. Up to 60 wt % of the deoxygenation of the lignite/vacuum bottoms occurs at relatively low severity but the slope of the deoxygenation line is low indicating that once relatively weak functional groups such as $-COOH$ and $-OH$ are removed, the removal of oxygen becomes more difficult. Desulphurisation appears to require higher severity than deoxygenation. However it proceeds rapidly with further increase in process severity. Hydrogenation appears to be less dependent on process severity than heteroatom removal. Broken lines represent data for the subbituminous coal. The be-

haviour of the Saskatchewan lignites and the Alberta subbituminous coal is similar. It should be noted that the hydrogenation of the slurry at low pitch conversion is significant, it is almost equal to that at high pitch conversion. The subbituminous coal runs showed a sharp increase in hydrogenation from 0 to 20 wt % pitch conversion and a gentle decrease from 20 to 40 wt % pitch conversion. The hydrogenation increases monotonously with pitch conversion above 40 wt %, where hydrocracking begins to dominate the coprocessing reaction.

Table 3 shows product characteristics from selected runs at various operating conditions. It can be seen that when the process severity is increased a significant upgrading of the distillates takes place.

Table 4 compares the properties of distillates produced by typical coal liquefaction processes, (i.e., SRC and H-coal), straight petroleum No. 6 fuel oil, and coprocessing distillates. It should be noted that the coal liquefaction products were derived from Illinois No. 6 coal but operating conditions of these processes are unknown, hence all the properties in Table 4 are for approximate comparisons only (7). Simulated distillation shows that the boiling points of distillates from coprocessing are lower than those of No. 6 fuel oil. The H/C ratios of coprocessing products are similar to the H/C ratio of No. 6 fuel oil. The oxygen contents in the coprocessing products are considerably higher than those of No. 6 fuel oil, which is due to the very high oxygen content of the feed coals. While the aromaticity of coal derived products varies from 60 to 80, that of coprocessing distillates ranges from 25 to 35. Again the qualities of the coprocessing distillates are comparable to those of No. 6 fuel oil in this respect.

CONCLUSIONS

- Coprocessing of low-rank coals and vacuum bottoms is feasible.
- Coal and pitch conversions appear to increase linearly with increasing temperature over the range studied.
- Distillate and gas yields appear to increase linearly with increasing pitch conversion.
- Hydrogen (equivalent) consumption ranges from 2 to 3 wt % of slurry feed (maf).

- The qualities of distillates produced by the coprocessing of low-rank coals and vacuum bottoms are comparable to those of No. 6 fuel oil.

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Table 1 - Properties of feed coals and oil

COAL

Coal	Coronach	Bienfait	Plains
Province	Sask.	Sask.	Alberta
Rank	Lignite	Lignite	Subbituminous
<u>Proximate analysis (wt %)</u>			
Moisture	-	-	-
Ash	19.48	8.11	9.50
Volatile	39.96	43.68	42.06
Fixed carbon (By difference)	40.54	48.21	48.44
<u>Ultimate analysis (dry basis) (wt %)</u>			
C	55.43	65.94	64.04
H	3.66	4.46	3.87
S	1.13	0.69	0.53
N	0.89	1.48	1.65
Ash	19.48	8.11	9.50
O (By difference)	19.41	19.33	20.41

OILCold Lake Vacuum Bottoms

Specific gravity	1.04
Asphaltenes (wt %)	24.6
Preasphaltenes (wt %)	0.0

Distillates (525°C-)	17.0 wt %
Residue (525°C+)	83.0 wt %

Table 2 - Process performance

Run No.	Severity**	Coal	Pitch			Yields****		Hydrogen****
		<u>conversion</u> (wt %)	<u>conversion</u> (wt %)	C ₁ ~C ₄	H ₂ O	Distillate*	Residue	consumption
<u>Coronach</u>								
1	H	82.7	70.0	2.9	5.6	63.9	25.9	3.1
2	MH	73.8	54.5	3.1	4.5	52.7	39.2	2.2
3	M	70.8	34.0	1.8	4.7	34.3	56.5	2.9
4	L	57.7	12.4	0.7	3.4	20.6	75.4	-
5	H	73.8	70.2	4.8	5.2	65.6	25.7	2.6
6	H	84.0	69.0	4.6	5.3	62.8	27.0	1.6
<u>Bienfait</u>								
1	H	81.3	67.1	4.2	2.9	59.8	28.4	2.9
2	M	72.0	38.1	1.5	5.0	40.2	53.2	2.5
3	MH	73.7	50.7	1.9	4.9	53.5	42.6	2.6
4***	M	68.7	41.2	1.5	1.5	41.5	50.7	2.1 (H ₂ equiv.)
5***	MH	75.1	45.9	1.7	1.3	54.0	46.6	1.6 (H ₂ equiv.)

* Distillate excludes water and includes C₅₊ found in the exhaust gases

** H - High, MH - moderate/high, M - moderate, L - low

*** Synthesis gas run

**** wt % of the maf slurry feed

Table 3 - Product characteristics

<u>Feeds</u>						
Oil	Cold Lake vacuum bottoms					
Coal	Coronach			Bienfait		
Run No.	1	3	4	1	2	
Severity	High	Moderate	Low	High	Moderate	
<u>Distillate</u>						
Yield* (wt %)	63.9	34.3	20.6	59.8	40.2	
Specific gravity	0.893	0.923	0.939	0.885	0.916	
gravity						
H/C ratio	1.67	1.64	1.53	1.65	1.63	
Aromaticity (%)	25	25	32	26	26	
<u>Yields of distillate fractions* (wt %)</u>						
Naphtha (IBP-205°C)	22.0	5.3	2.9	15.2	5.3	
LGO (205-335°C)	11.8	9.6	3.0	20.7	12.9	
HGO I (335-415°C)	17.0	7.7	6.0	11.3	8.3	
HGO II (415-525°C)	13.1	11.7	8.8	12.6	13.7	
<u>Residue</u>						
Yields*	25.9	56.5	75.4	28.4	53.2	
H/C ratio	1.06	1.20	1.28	0.96	1.15	
<u>Yields of residue components* (wt %)</u>						
Residual oil	14.0	33.3	43.5	15.1	28.0	
Asphaltenes	6.1	14.2	16.2	7.1	13.7	
Preasphaltenes	0.4	0	2.7	0.2	2.7	
THF insolubles (ash free)	5.2	9.0	13.1	6.0	8.9	

* Based on maf slurry feed

Table 4 - Comparative properties of various coal liquids, No. 6 fuel,
and coprocessing product

Constituent	SRC ^a	H-coal ^a	Petroleum	Coprorocessing (high severity, distillate only)		
			No. 6 fuel oil	Coronach ^b	Bienfait ^c	Subbituminous C
C	87.9	89.0	86.4	85.06	84.25	85.60
H	5.7	7.9	11.2	11.81	11.55	10.56
O	3.5	2.1	0.3	1.60	1.93	1.42 ^d
N	1.7	0.77	0.41	0.31	0.38	0.80
S	0.57	0.42	1.96	1.31	1.46	1.62
Ash	0.11	0.02	0.68	0.0	0.0	0.0
<u>Fraction (Vol %)</u>			<u>Simulated distillation (°C)</u>			
IBP	510	250	175	123	128	108
15	>510	312	-	-	-	-
20	>510	327	379	220	208	208
50	>510	404	478	315	304	321
70	>510	>517	>532	372	368	385
90	>510	>517	>532	412	408	431
Aromaticity (%)	77	63	24	25	26	33
H/C ratio	0.78	1.07	1.56	1.67	1.66	1.48

a) Liquid derived from Illinois No. 6 coal, operating conditions unknown (7)

b) Run No. 1; c) Run No. 1; d) By difference

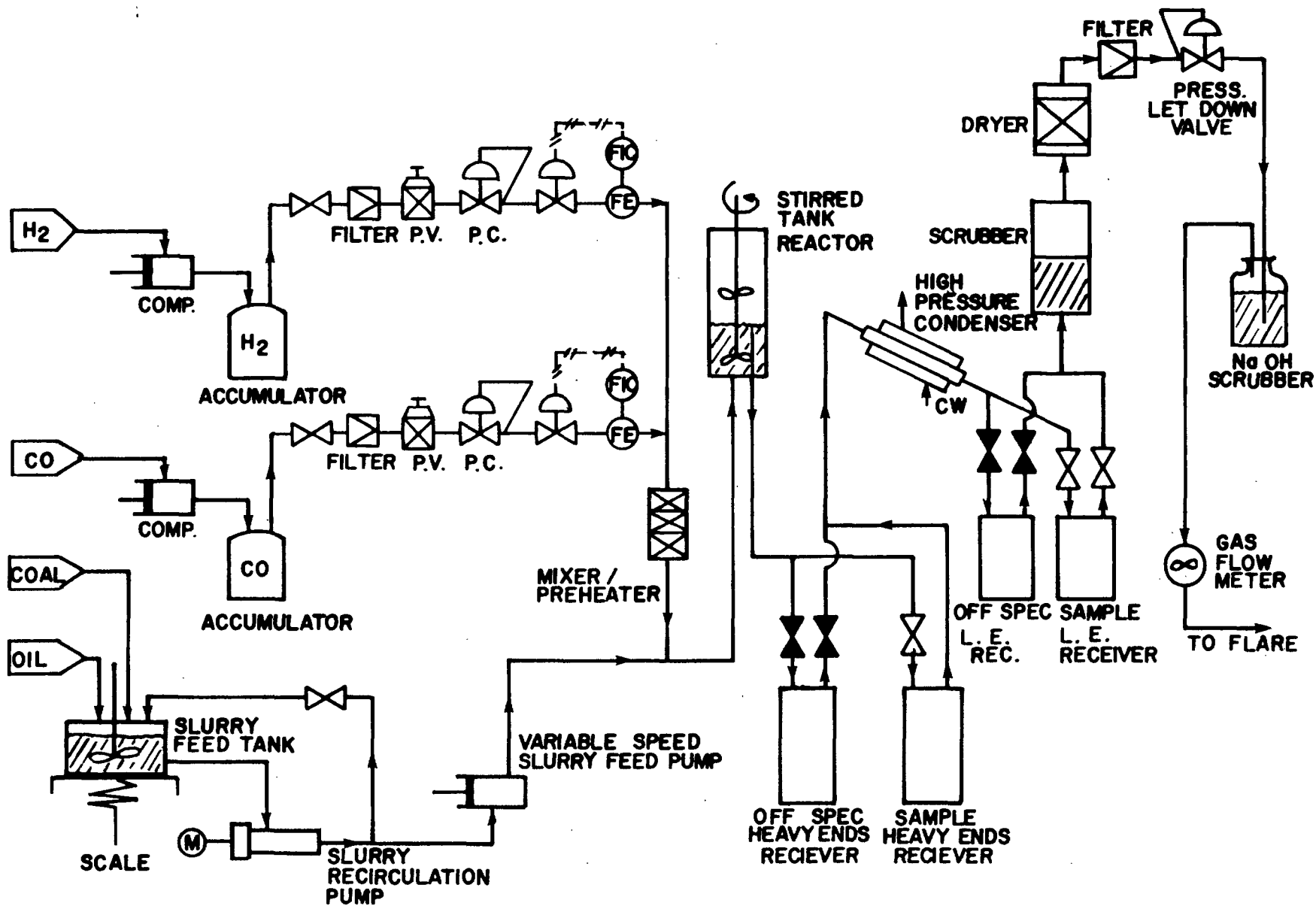


Fig. 1 CANMET CONTINUOUS FLOW COPROCESSING UNIT

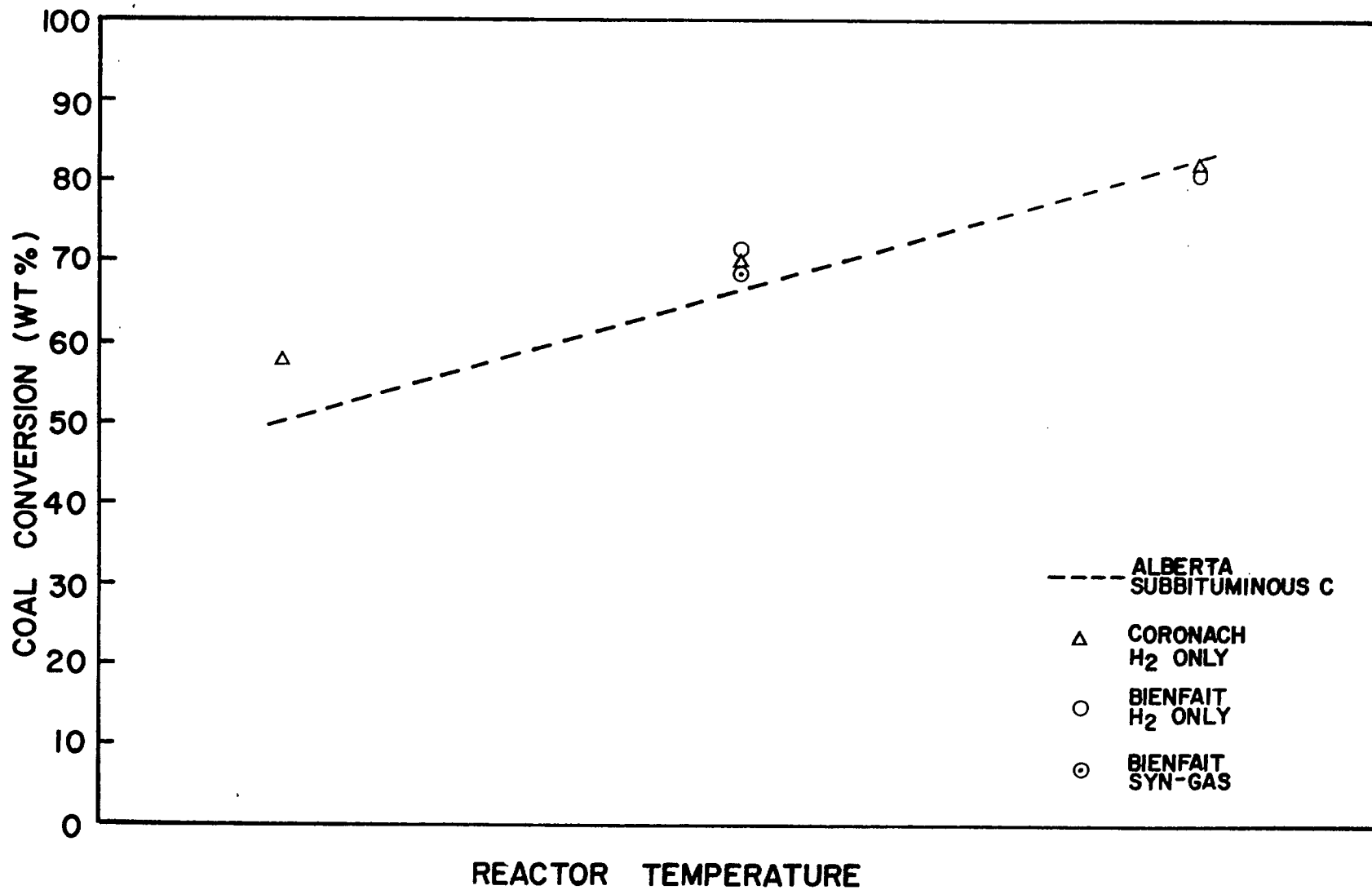


Fig. 2 COAL CONVERSION VS. REACTOR TEMPERATURE

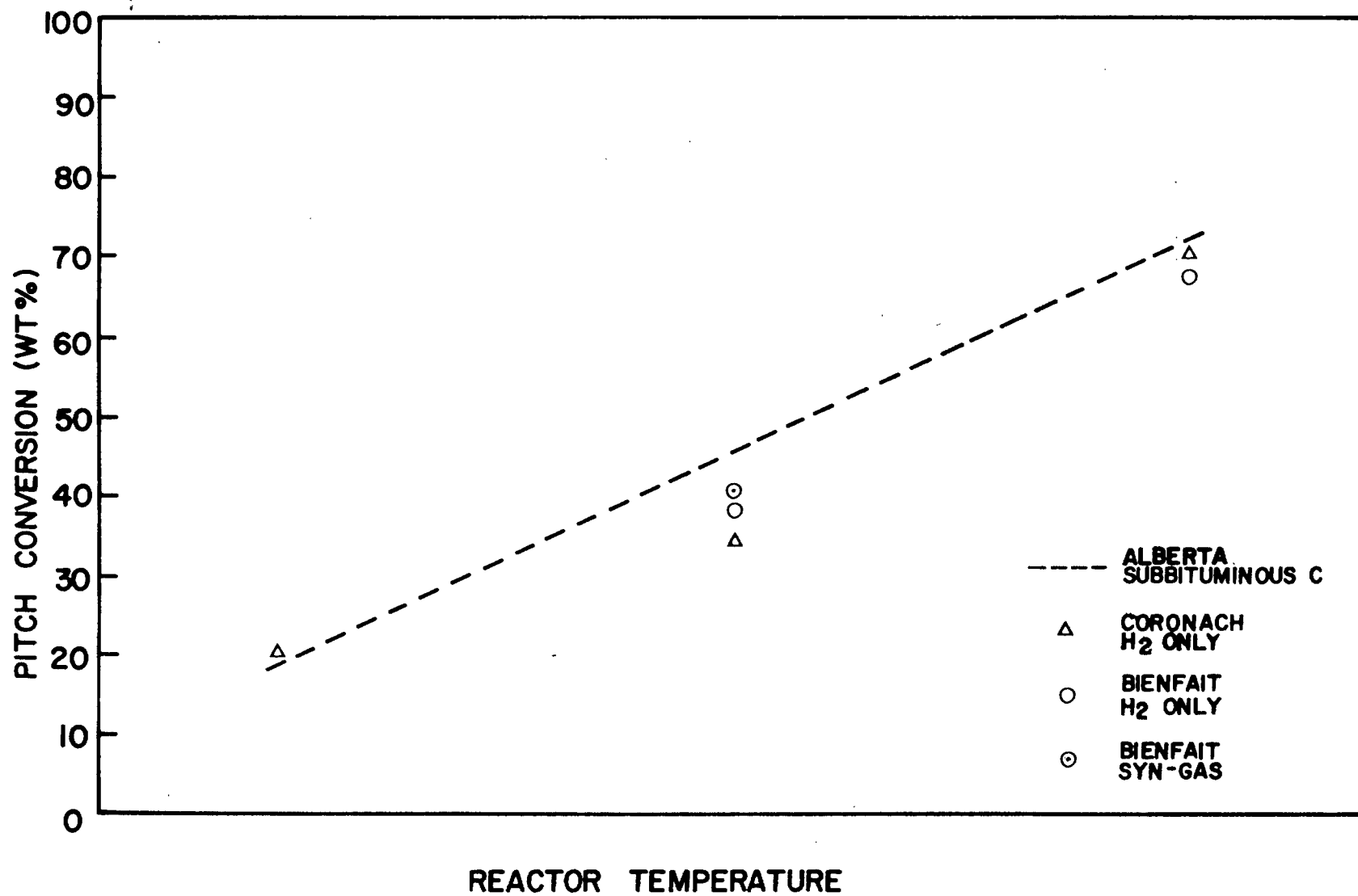


Fig. 3 PITCH CONVERSION VS. REACTOR TEMPERATURE

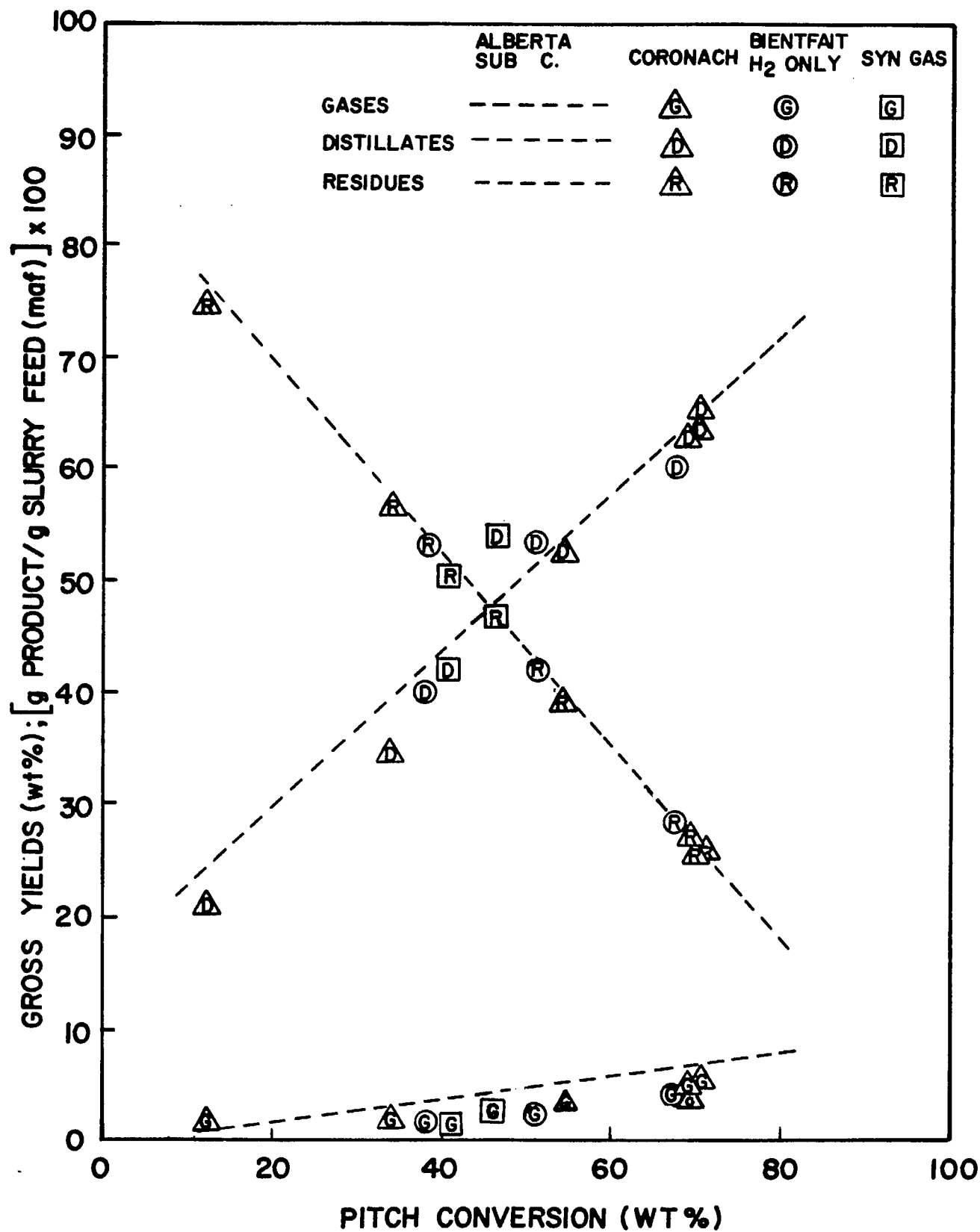


Fig. 4 GROSS YIELDS VS. PITCH CONVERSION

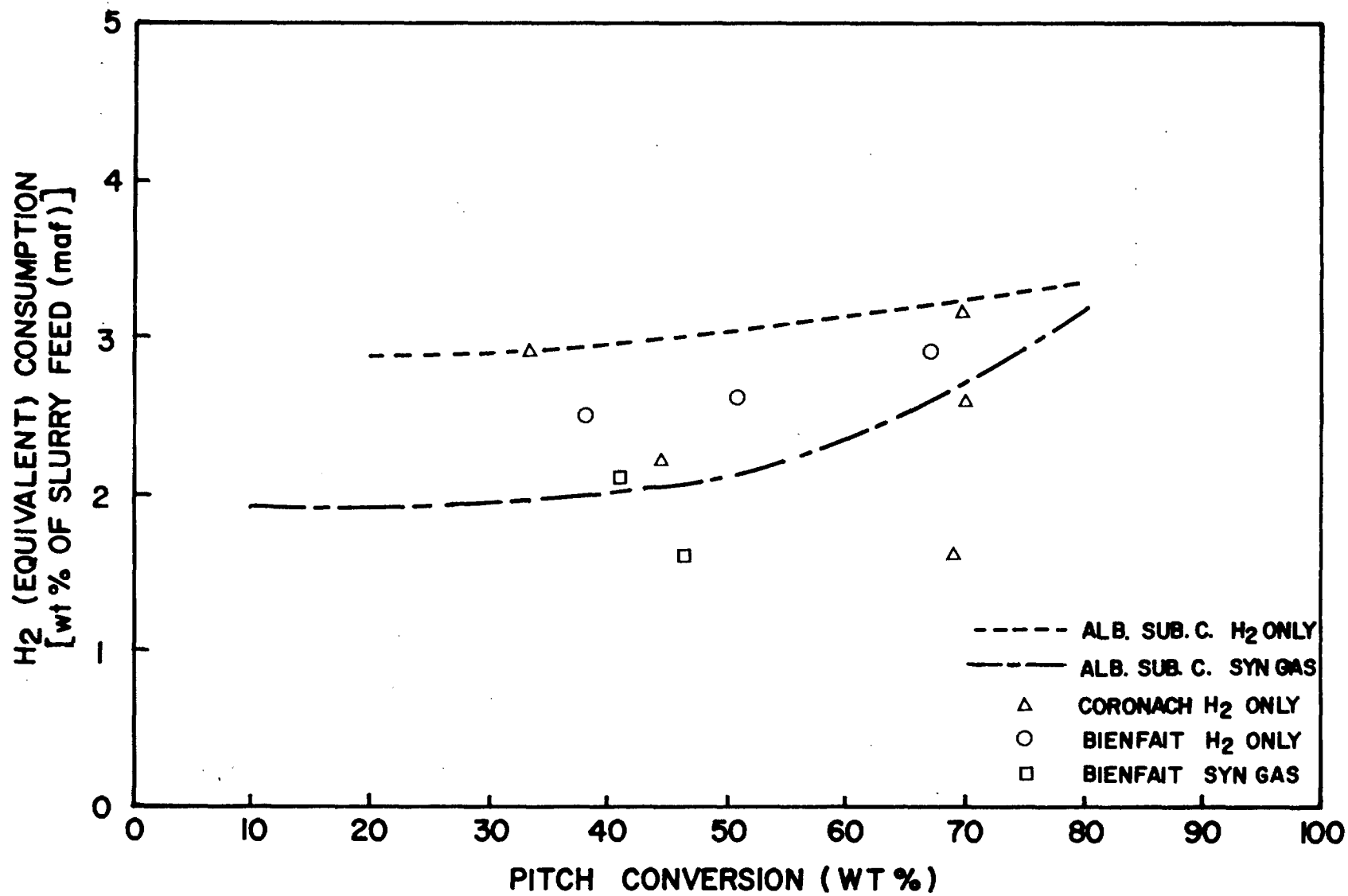


Fig. 5 HYDROGEN EQUIVALENT CONSUMPTION VS. PITCH CONVERSION

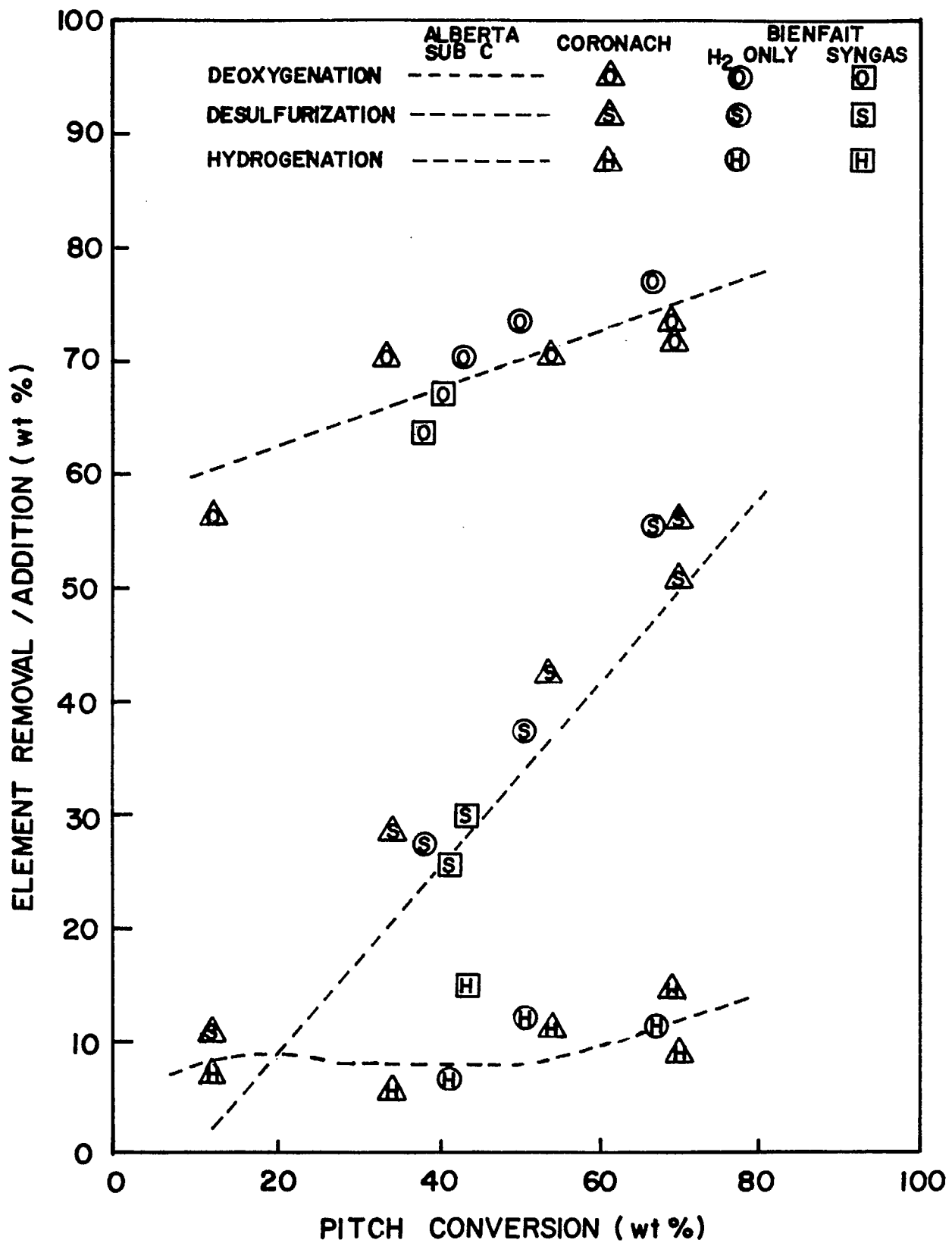


Fig. 6 HETEROATOM REMOVAL & HYDROGEN ADDITION VS. PITCH CONVERSION