Appendix B

Computer Model for Predicting Wax Hydrocracking Product Distribution

A theoretical model was developed based on a set of hydrocracking rules described in the literature by Archibald et al. The rules were developed based on the hydrocracking mechanism for a n-alkane or normal paraffin (Figure B.1).

Pure component studies have suggested that the mechanisms of hydrocracking normal paraffins involves a carbonium ion intermediate for the cracking of carbon-carbon bonds, coupled with the chemistry of hydrogenation. The reaction path for paraffins initiates at the metallic component of the catalyst with the formation of an olefin by dehydrogenation. The olefin is then rapidly adsorbed on an acid site to form a carbonium ion that subsequently isomerizes to a more stable carbonium ion, or cracks at the beta position to form another cation and an olefin. Secondary cracking occurs as the carbonium ion continues to isomerize and crack, while the olefin is saturated at the metallic site to form a paraffin.

Paraffin or straight chain n-alkane hydrocracking is the reaction of primary importance with Fischer-Tropsch waxes. Fischer-Tropsch Arge wax closely represents a mixture of n-alkanes with a wide distribution of carbon numbers. This distribution poses a problem in modeling wax hydrocracking as each alkane will have a different reaction rate for each step in the mechanism. Before the modeling approach is described, the different analytical procedures used to determine hydrocracking product distribution must be discussed.

B.1 ANALYTICAL PROCEDURES TO MEASURE PRODUCT SELECTIVITY

- Gas chromatography (GC) simulated distillation gives product distribution on the basis of the boiling range.

- Oldershaw fractionation is much more representative of commercial distillation.

- Gel permeation chromatography (GPC) yields carbon number distribution. Neither GC nor Oldershaw methods give relative amounts of each carbon number product. GPC data will be used in the wax hydrocracking model development as the model predictions are based on carbon number distribution.

The following are the inaccuracies in the GPC analyses:

- GPC is calibrated using different lengths of straight chain polyethylene but hydrocracking yields branched product.

- GPC stretches carbon number lengths -- C_{30} by GPC corresponds to a boiling endpoint of C_{23}. Branched isomers may be stretching the GPC data (Table B.1).

- GPC raw data are not available at exact carbon numbers and at regular intervals. Hence, raw GPC data must be smoothed using summing, differentiation and interpolation. After smoothing, the data are normalized to account for the light C_6- products. Figure B.2 shows the end result of the process of converting raw GPC data to total carbon number distribution; a more meaningful distribution to represent pilot plant product yield data. The discontinuity at C_6/C_7 is due to GPC stretching C_{7+} branched molecules toward higher carbon numbers while GC accurately represents C_6- branched molecules.

In spite of the inaccuracies of GPC product analyses, the results are directionally consistent with other methods. Absolute yield measurements might be inaccurate, but product yields by GPC can be used for model development and model calibration. Figures B.3 through B.6 show total carbon number distribution by GPC from pilot plant runs at various process conditions.

Figure B.6 shows that CFR had the greatest effect on product yield selectivity.

B.2 WAX HYDROCRACKING MODEL DEVELOPMENT

An attempt was made to model wax hydrocracking based on rules developed for n-alkane hydrocracking. The starting point was a set of hydrocracking rules described by Archibald et al.

B.2.1 Archibald Rules (Model A)

A theoretical model was developed based on a set of hydrocracking rules described by Archibald et al. The rules are based on the hydrocracking mechanism for straight chain alkanes shown in Figure B.1.

The Archibald rules for hydrocracking paraffins are:

- Only alkanes larger than C_6 may be cracked.
- C_3 is the smallest product molecule
- β scission of carbon-carbon bonds giving C_3 products is half the probability of other bonds.
- All other carbon-carbon bonds have equal probability of β-scission.

The following assumptions are inherent in the rules:

- The rules apply to a mixture of alkanes, with one chain length having no effect on another. Also, the rules assume all molecular lengths will hydrocrack with equal probability. The reaction rates of molecules of different length are assumed equal.

- The rules assume no isomerization reactions during hydrocracking (not true, especially with an acidic catalyst).

- Operating variables such as liquid hourly space velocity (LHSV), pressure, hydrogen recycle rate and catalyst type are not included in the model. Combined feed rate (CFR) was the only variable modeled.

Figure B.7 shows product carbon number distribution using the model developed from the Archibald rules. Although the model shows large differences in product selectivity between 1.0 and 1.5 CFR, the model does not reflect actual pilot plant data. The next figure B.8 shows the modeling results on an expanded Y-scale. Only at extremely high CFR's, does the model approach pilot plant data. The Archibald rules for wax hydrocracking yield very poor distillate (300-700°F) selectivity and do not accurately predict pilot plant results. The reasons for the model not working well may be due to the assumptions: all molecules crack with equal probability, there is no isomerization and no influence of kinetic parameters, such as temperature and liquid hourly space velocity.

B.2.2 Modified Archibald's Rules (Model C)

In the Archibald rules, the molecules must crack at the beta position relative to a carbonium ion. A carbonium ion can form with equal probability at every secondary carbon atom. Hence, cracking can occur at any carbon- carbon bond as long as at least a C_3 length product results.

To improve distillate yield in the model, Archibald rules were modified so that a molecule could crack only at the carbon atom closest to the center of the molecules. Also, the computer program was modified to hydrocrack the largest feedstock molecules first. Figure B.9 shows that this approach gives the best distillate yield. The distillate yields, however, are greater than those obtained in the pilot plant for either the once-through or the recycle case.

B.2.3 Molecular Length Bias (Model AB)

A combination of two approaches was next used in the wax hydrocracking model. In this approach, the largest molecules hydrocracked in the center and the smaller molecules larger than C_6 hydrocracked by the Archibald rules. In the model, a bias could be introduced to change the relative proportion of molecules that are hydrocracked for a certain carbon number. Figure B.10 shows different methods of biasing the amount of molecules that are hydrocracked for a carbon number. The bias can be linear or nonlinear.

Figure B.11 shows the best fit, using the model, of the once-through pilot plant data. A combination of hydrocracking large molecules in the center and biasing the hydrocracking of smaller molecules by Archibald's rules was used to achieve this fit.

B.3 MODELING CONCLUSIONS

The model has shown that large molecules hydrocrack very easily. For the model to be more useful and for future modeling direction, kinetic factors such as temperature, liquid hourly space velocity and relative rate constants for molecules of different carbon lengths must be introduced. Only then can the model be put in practice for other feedstocks and operating conditions.

Table B.1

Analytical Procedures

Stream	GC Boiling Range, °F	Carbon Numbers	
		n-Alkane Boiling Points	GPC
Naphtha	C_7-300	C_7-C_9	C_7-C_{10}
Jet Fuel	300-550	C_{10}-C_{16}	C_{11}-C_{18}
Diesel	550-700	C_{17}-C_{23}	C_{19}-C_{30}

Figure B.1

Hydrocracking Mechanism

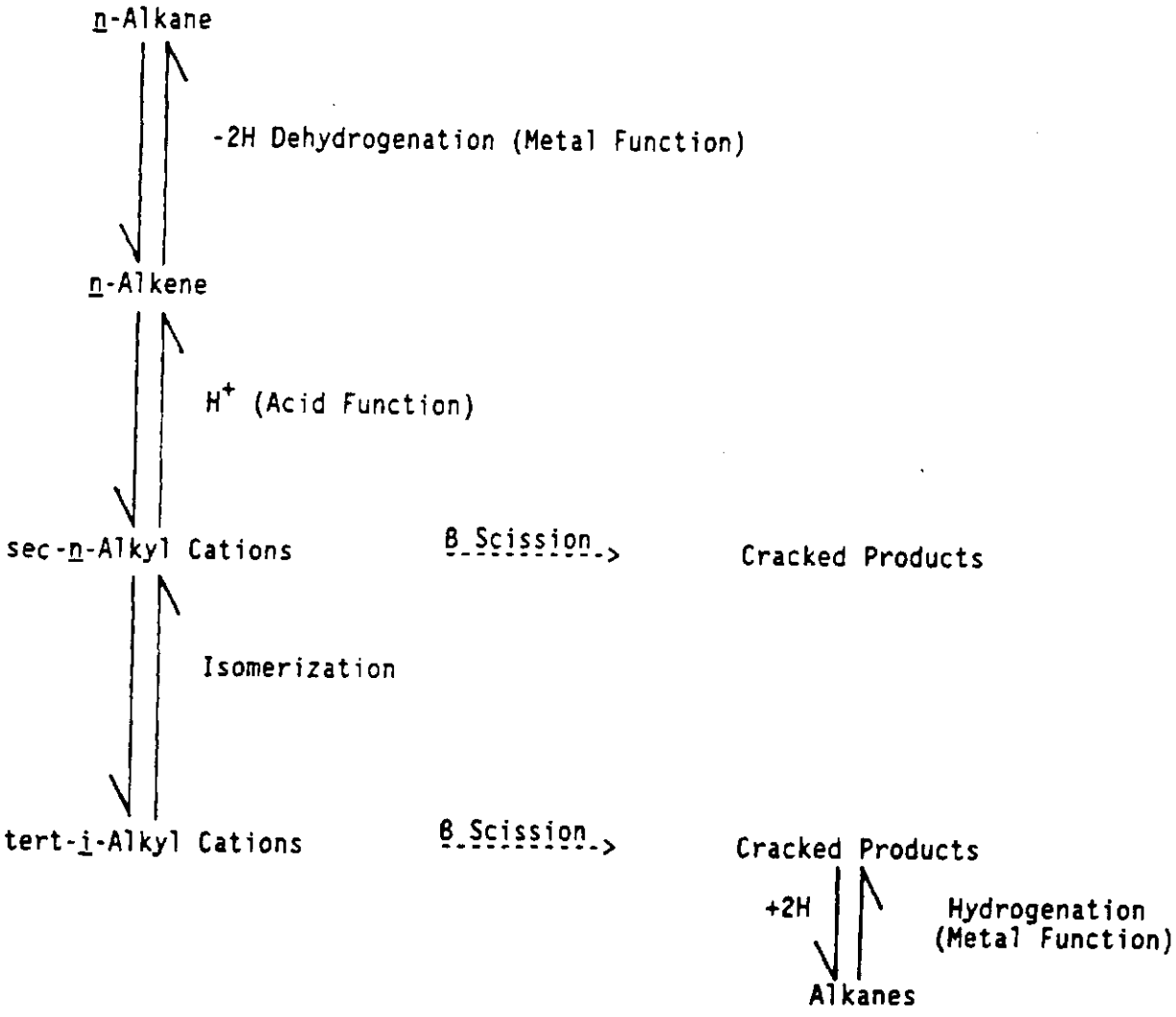


Figure B.2

GPC DATA WORKUP

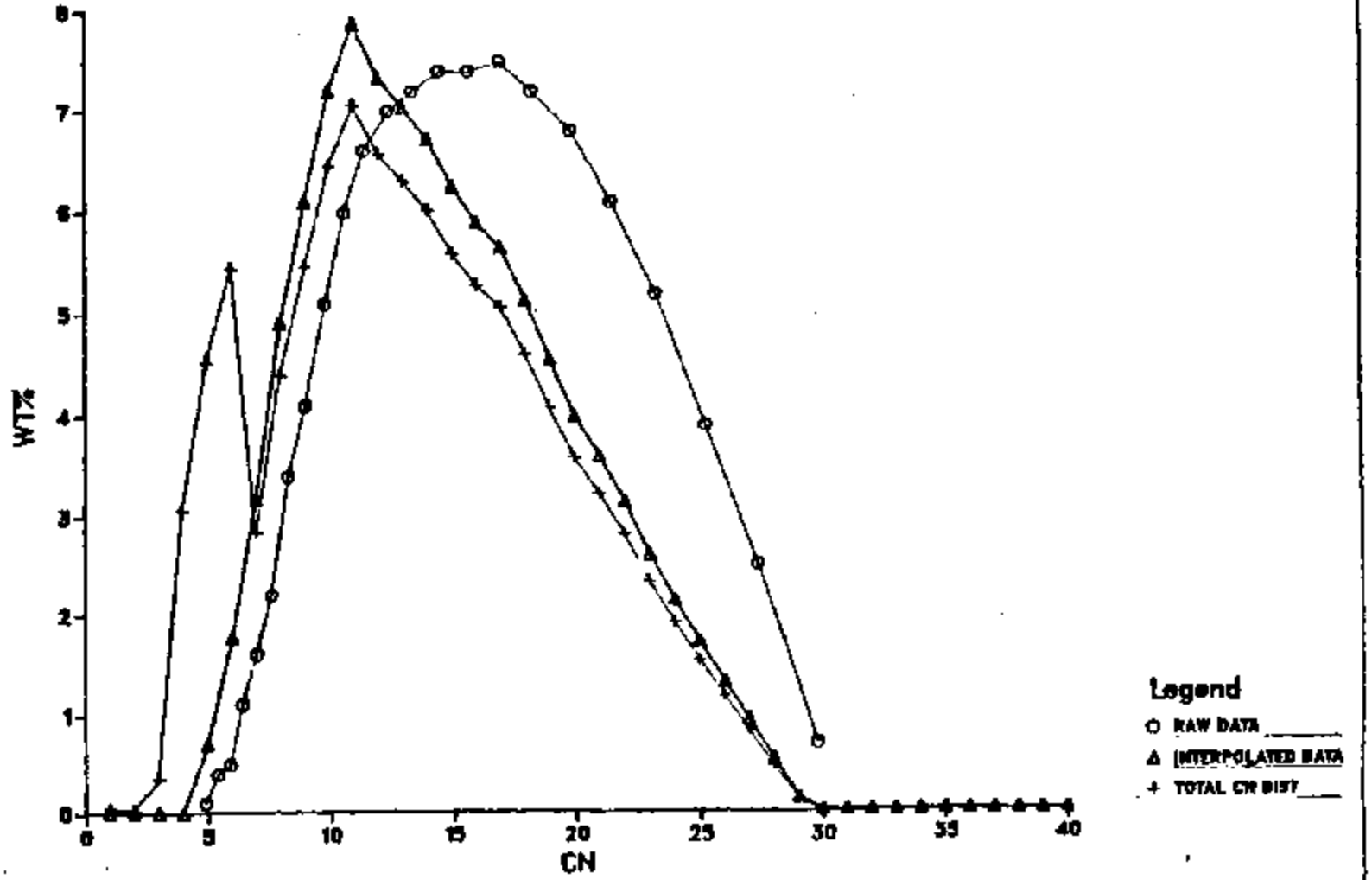


Figure B.3

FISCHER–TROPSCH WAX HYDROCRACKING

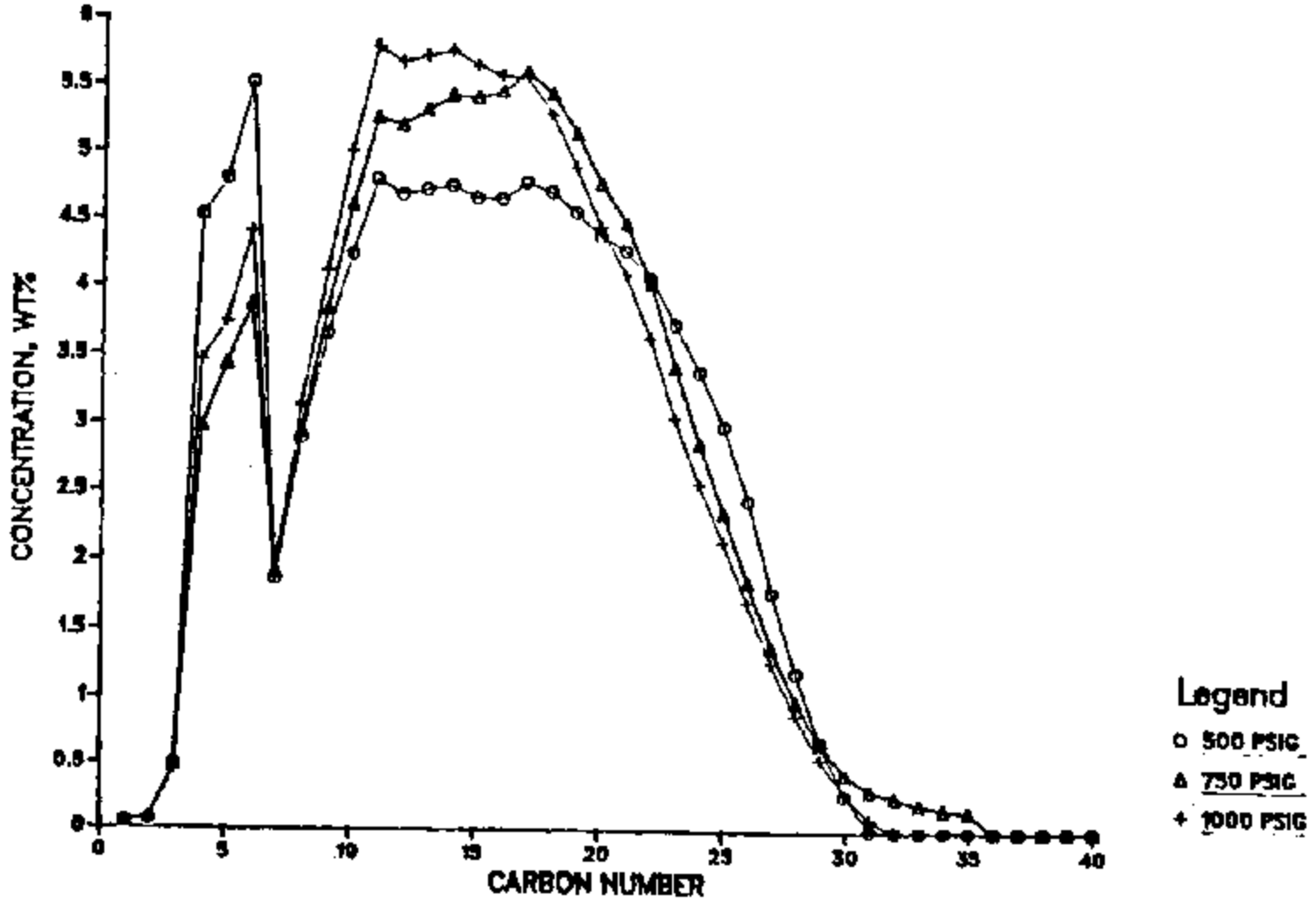


Figure B.4

FISCHER–TROPSCH WAX HYDROCRACKING

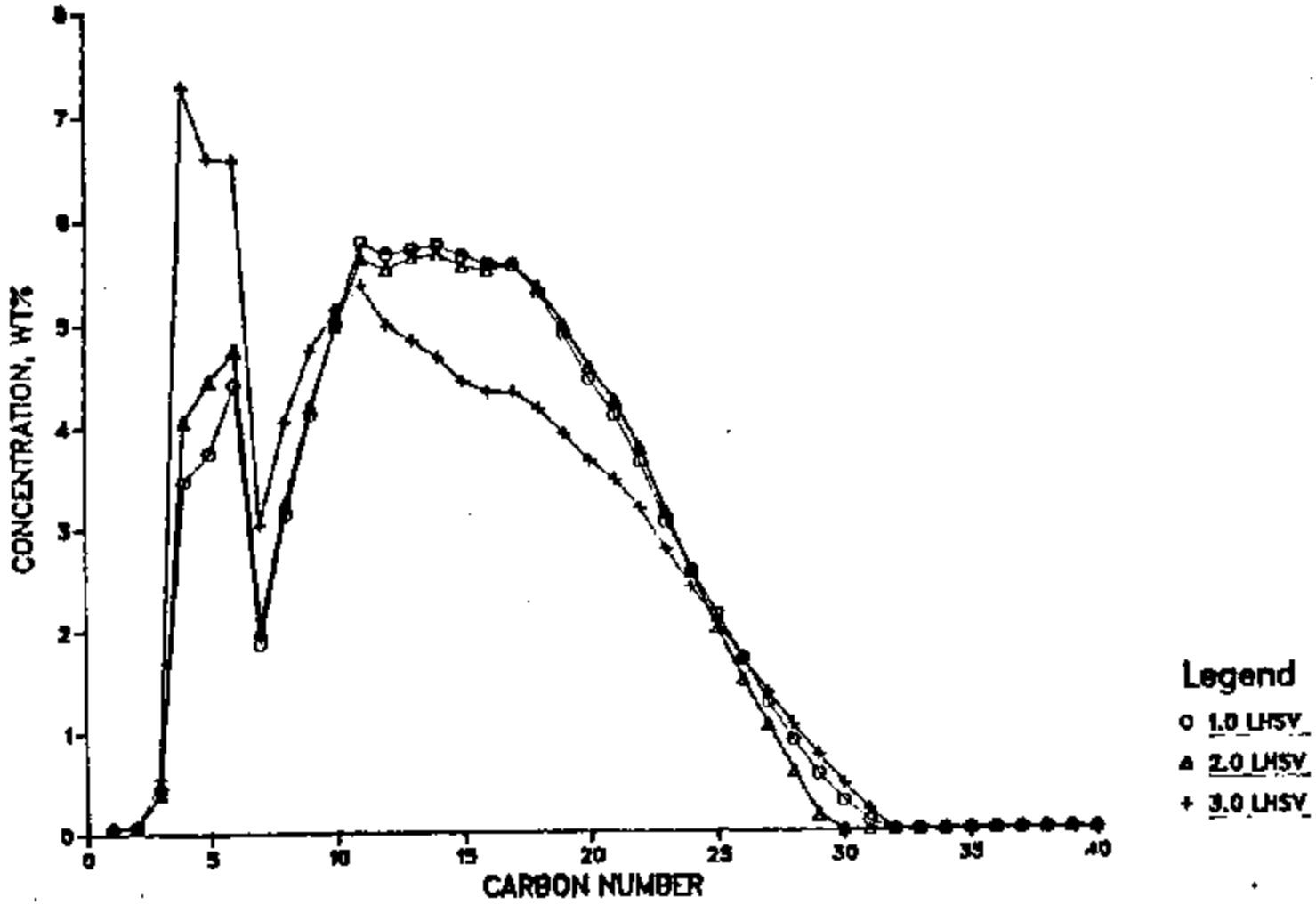


Figure B.5

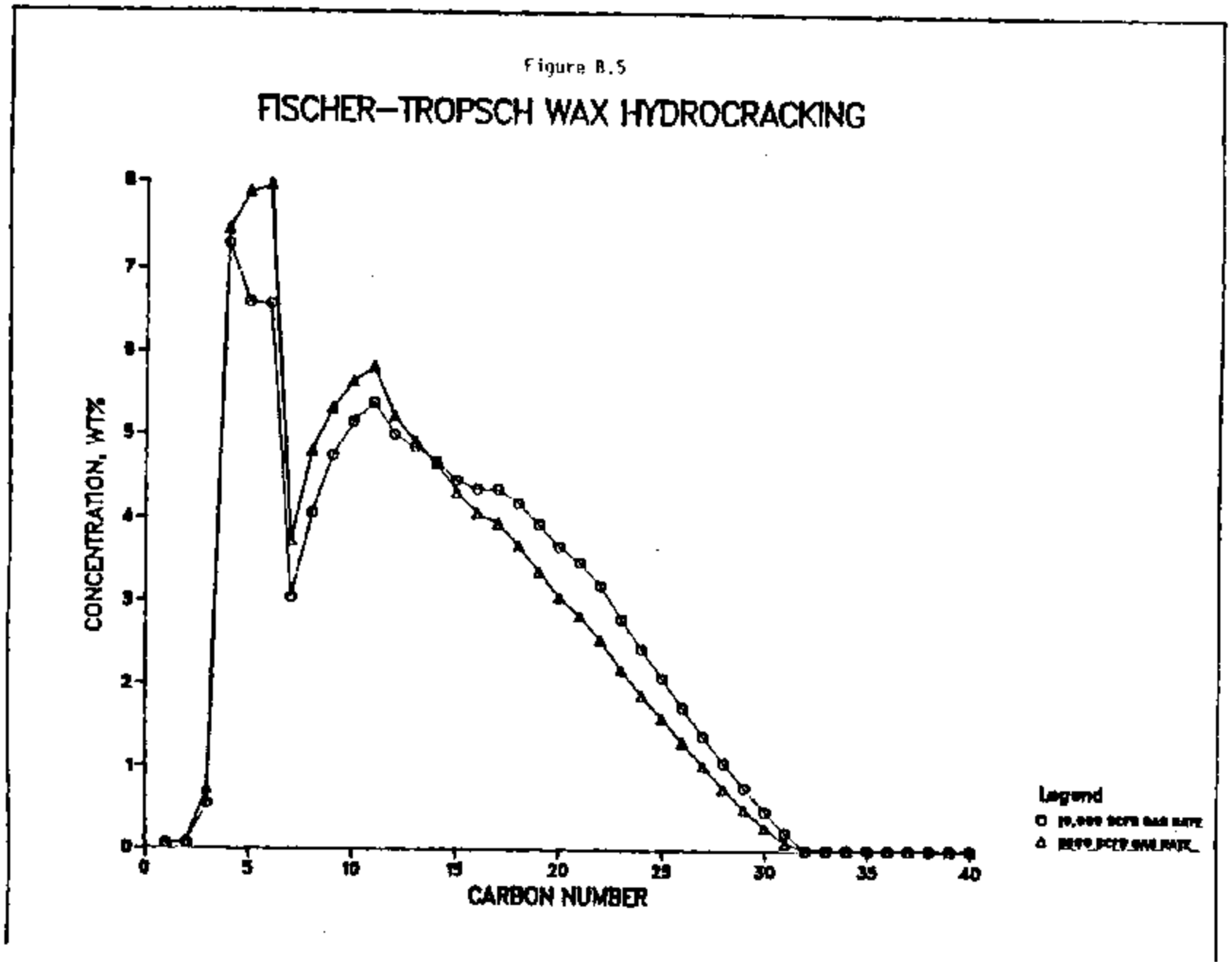

FISCHER–TROPSCH WAX HYDROCRACKING
CONCENTRATION, WT%
CARBON NUMBER
0
1
2
3
4
5
6
7
8
0
5
10
15
20
25
30
35
40
Legend

Figure 8.6

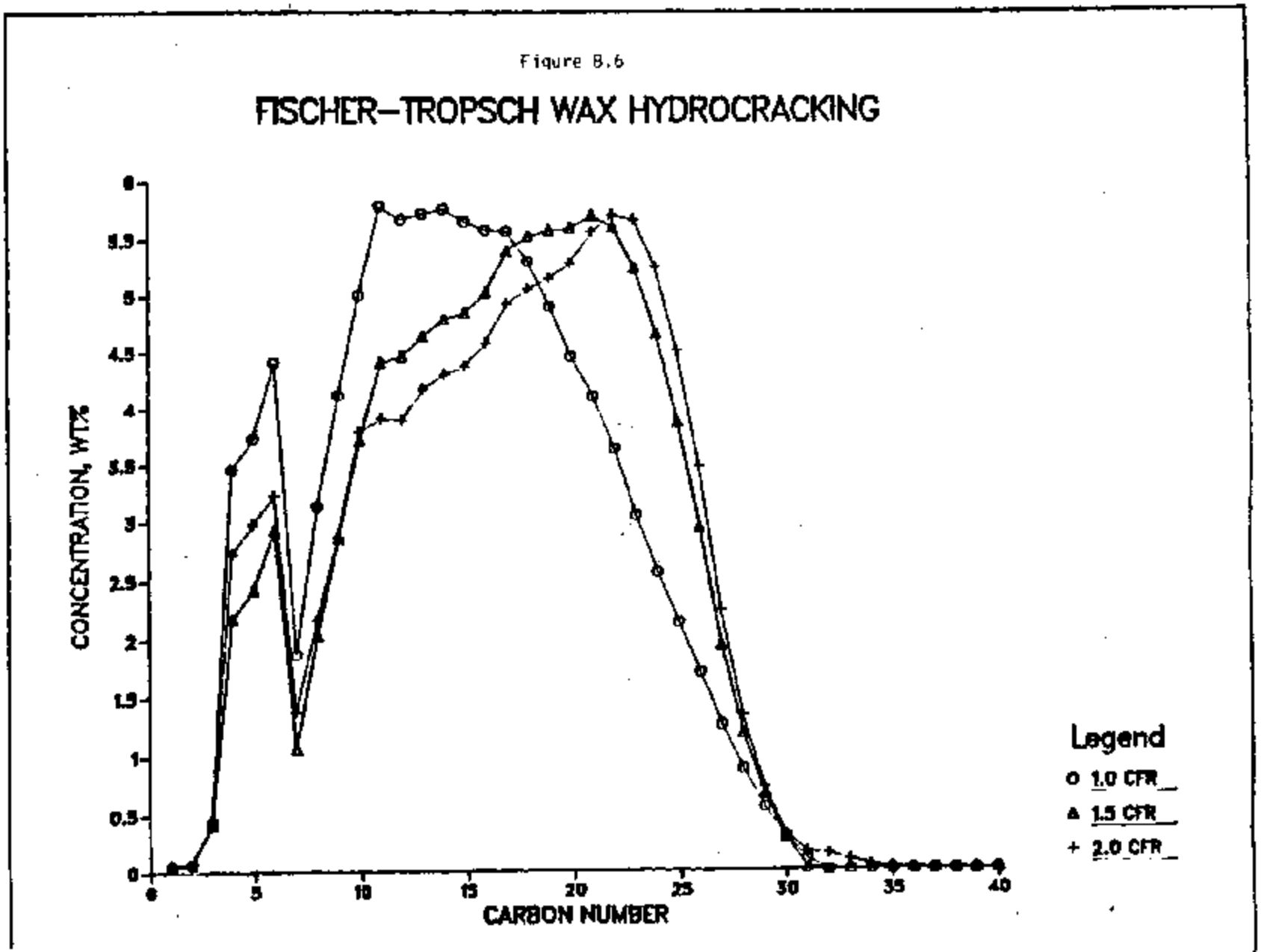

FISCHER–TROPSCH WAX HYDROCRACKING
CONCENTRATION, WT%
CARBON NUMBER
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
5.5
6
0
5
10
15
20
25
30
35
40
Legend
o 1.0 CFR
▲ 1.5 CFR
+ 2.0 CFR

Figure B.7

Wax Hydrocracking Model

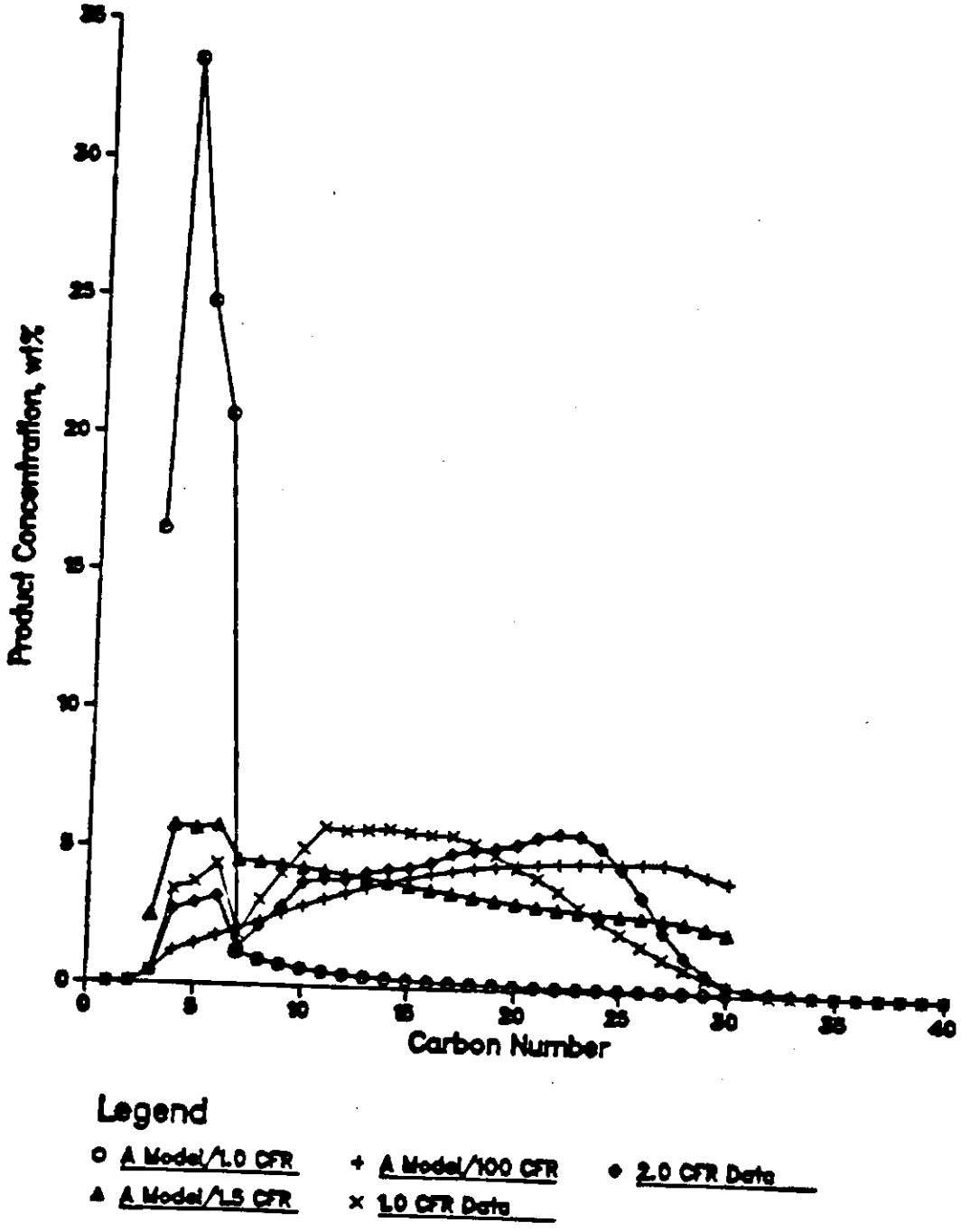


Figure 8.8

Wax Hydrocracking Model

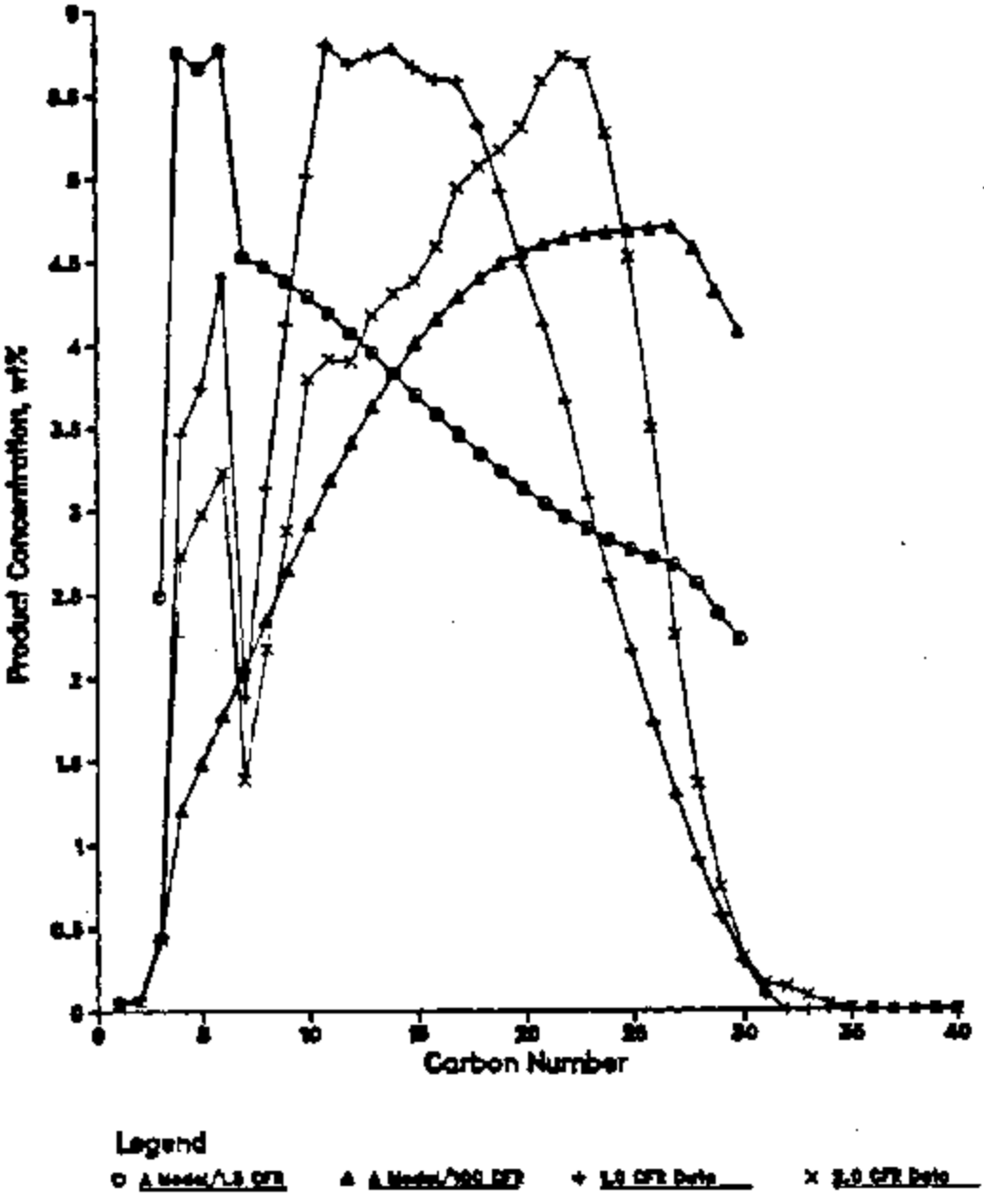


Figure B.9

Wax Hydrocracking Model

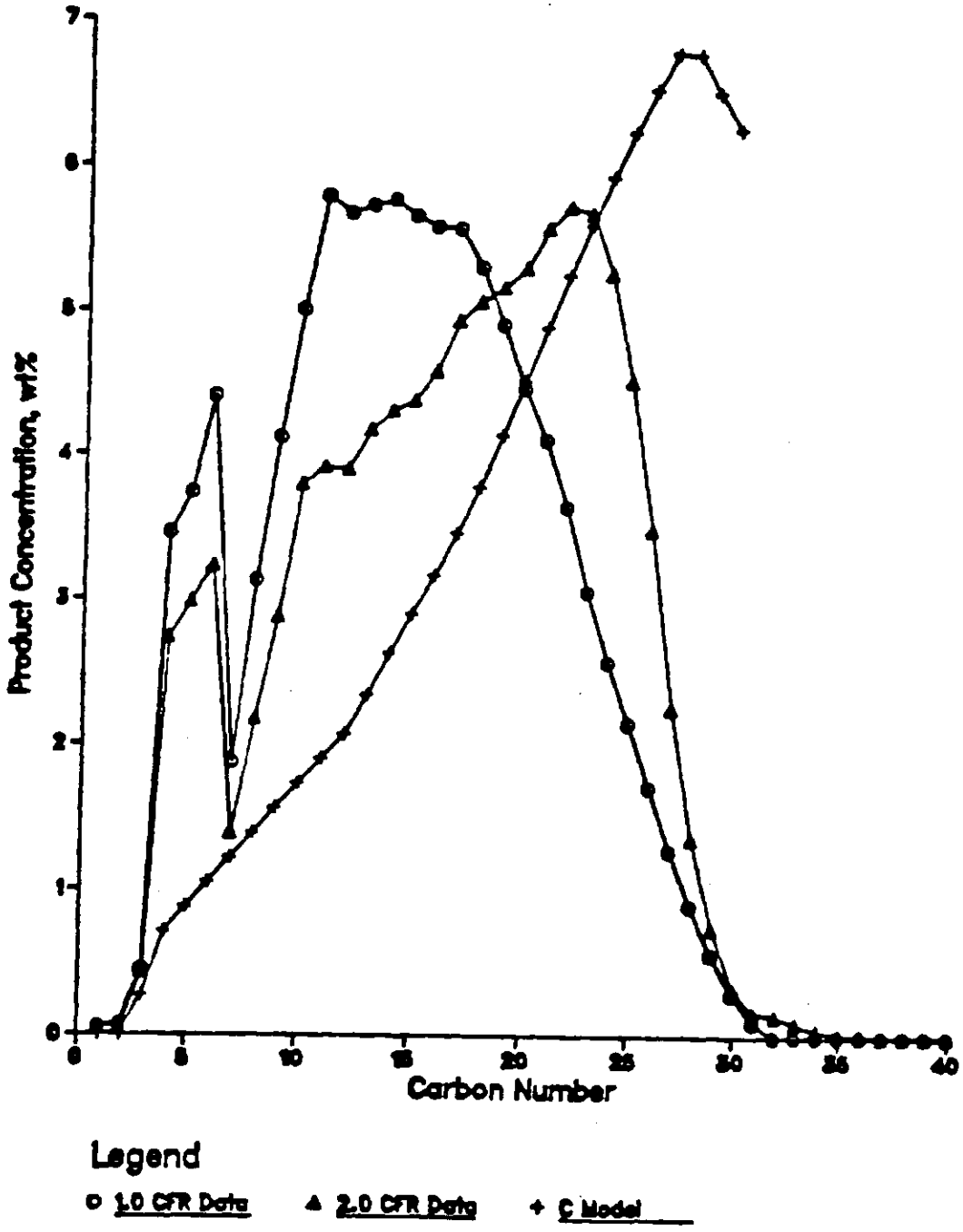


Figure B.1C

Wax Hydrocracking Model Feedstock Factors

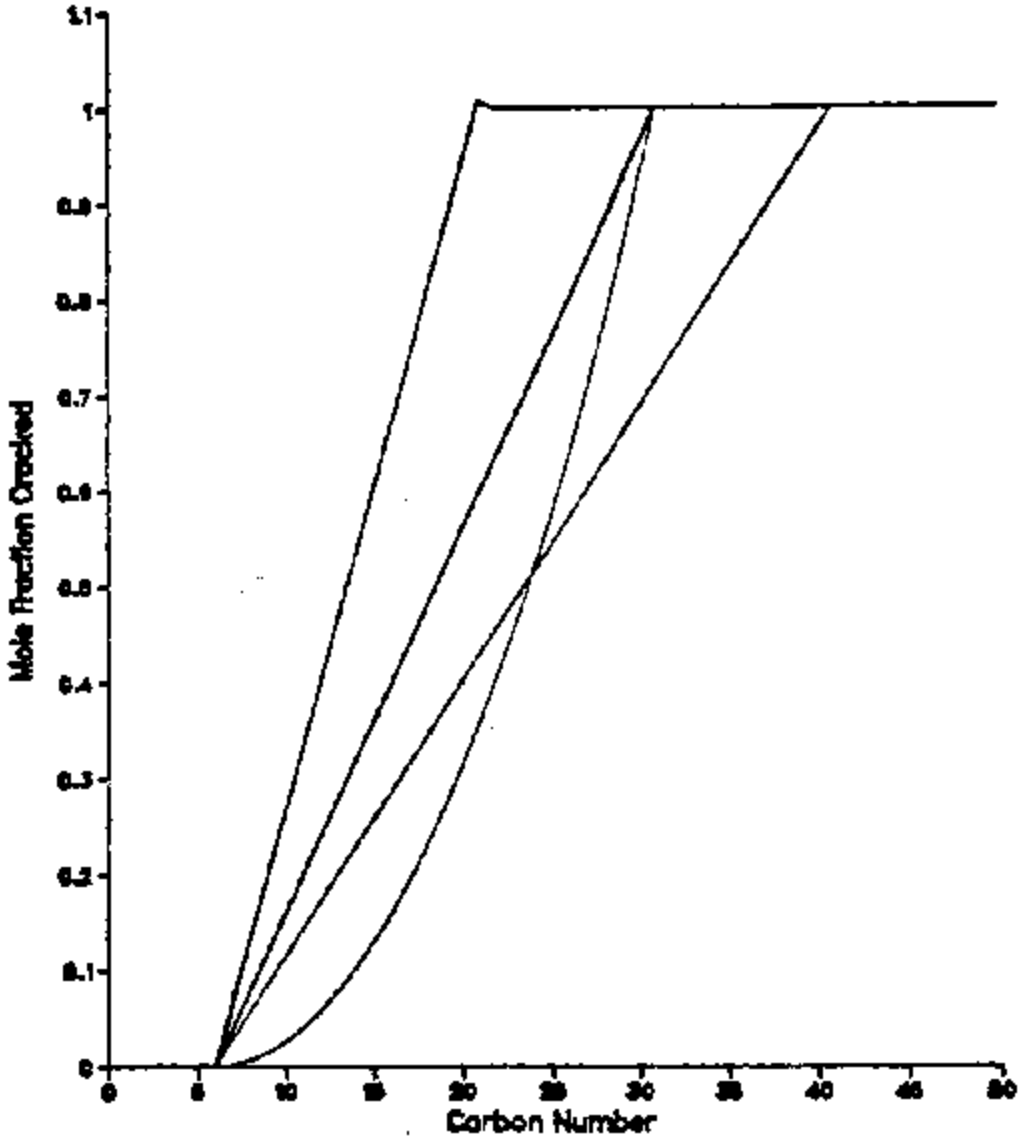
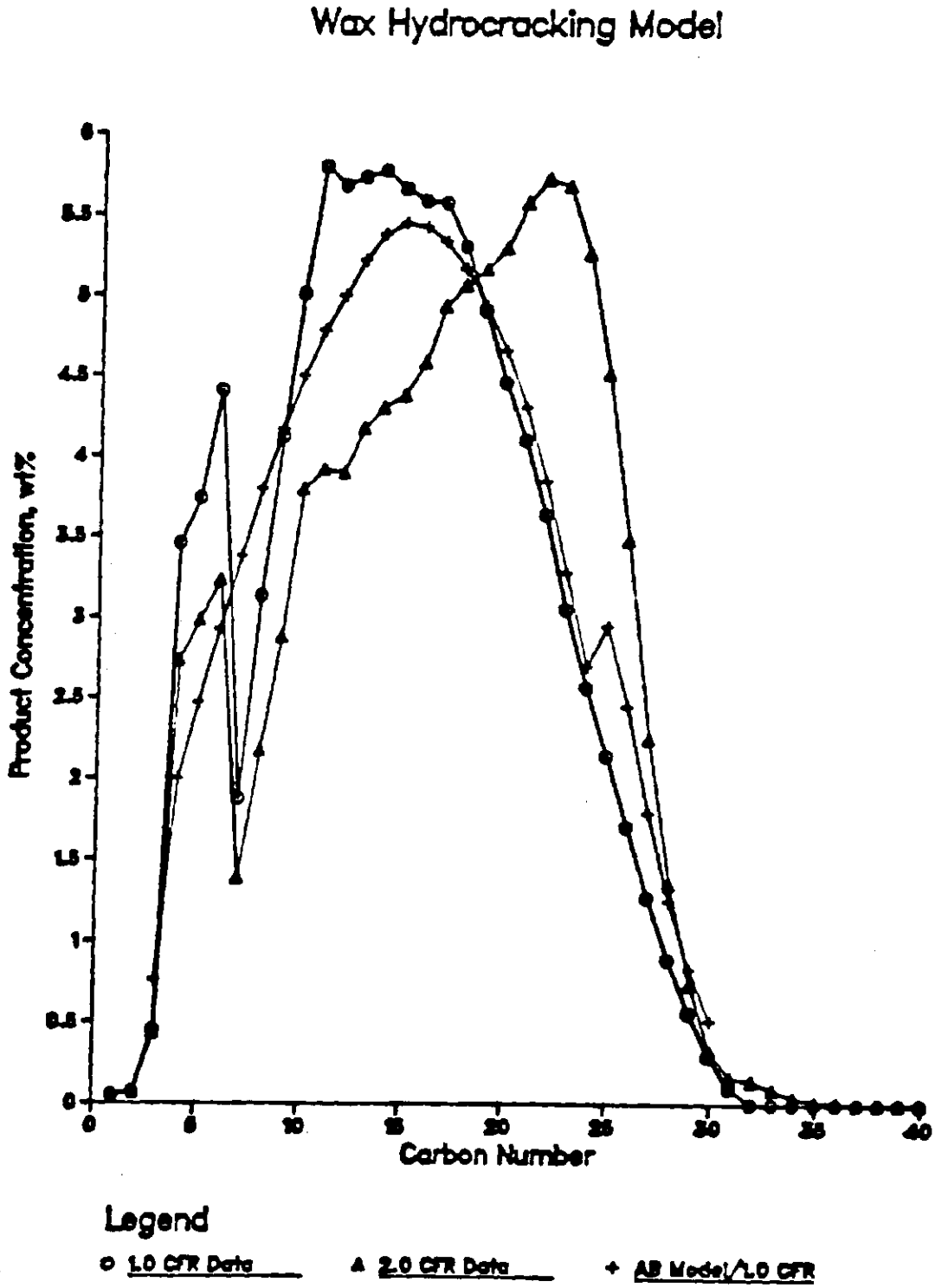


Figure B.11


Wax Hydrocracking Model
Product Concentration, wt%
Carbon Number
0
5
10
15
20
25
30
35
40
Legend
1.0 CFR Data
2.0 CFR Data
AB Model/1.0 CFR