

Fischer–Tropsch synthesis: The formation of branched hydrocarbons in the Fe and Co catalyzed reaction

Buchang Shi, Robert A. Keogh, Burtron H. Davis*

Center for Applied Energy Research, University of Kentucky, 2540 Research Park Drive, Lexington, KY 40511, USA

Received 13 September 2004; received in revised form 8 February 2005; accepted 14 February 2005

Available online 18 April 2005

Abstract

It appears that differences in modeling the fraction of branched products in the early work can be traced to much different products being formed in the low and high temperature FTS conditions. In the present study, for low-temperature FTS, it has been shown that, while the fraction of branched products may vary with catalyst, for a given catalyst the fraction of branched products remains constant in the C₇–C₁₄ range. The fraction for C₄ is very similar to the one for the C₇–C₁₄ range for the products from eight runs, five with iron catalysts and three with cobalt catalysts. It is therefore concluded that at low-temperature FTS conditions the fraction of branched products does not vary significantly with carbon number. Essentially the same fraction of branched products are obtained using the data from the analysis of the sample as collected, after hydrogenation so that the alkenes are converted to alkanes, and after bromination to convert the alkenes to dibromides that elute from the g.c. column at much longer times than the same carbon number alkanes. Thus, it is concluded that the fraction of branching in the alkene products is the same as in the alkane products.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Fischer–Tropsch synthesis; Hydrocarbons, branched; Catalyst, iron; Catalyst, cobalt; Isoparaffins

1. Introduction

To fully understand the mechanisms for the FTS reactions, it is important to understand how branched alkanes and alkenes are formed. If they are the products of secondary reactions, the question to be answered is how and under what conditions they are produced. On the other hand, if they are the primary products of the FTS reaction, then it is necessary for any mechanistic scheme proposed for FTS to include a pathway for the formation of branched alkenes and alkanes. In this study, we want to define the amount of branched hydrocarbons being formed under different conditions and with different catalysts to understand which factor or factors play the important roles in the formation of the branched products.

von Weber [1] appears to be the first to describe a regular increase in branched isomer content of FTS products with increasing carbon number and proposed the idea that this was

due to a definite probability of branching with each carbon addition to a growing chain. Later, workers at the U.S. Bureau of Mines provided a quantitative model to describe the formation of branched products from FTS [2]. Based on a mechanism of one carbon growth, they indicated that a carbon could add at the terminal or the penultimate position of either end of the chain so long as it did not produce either a quaternary carbon or an ethyl group. They considered the probability of adding a carbon at either position to be independent of chain length and that the distribution of isomers in the final product was identical with the distribution on the catalyst surface. The authors indicated that the results are not modified if they incorporate the assertion by Anderson [3] that carbon adds in proportion to the number (weighted) of ways that addition can occur to the individual isomers [4]. The calculations in these two references were compared to products obtained from low pressure synthesis with a cobalt catalyst.

Bruner [5] analyzed the products from the Hydrocol Process (high temperature synthesis with an iron catalyst in a

* Corresponding author. Tel.: +1 859 257 0251; fax: +1 859 257 0302.
E-mail address: davis@caer.uky.edu (B.H. Davis).

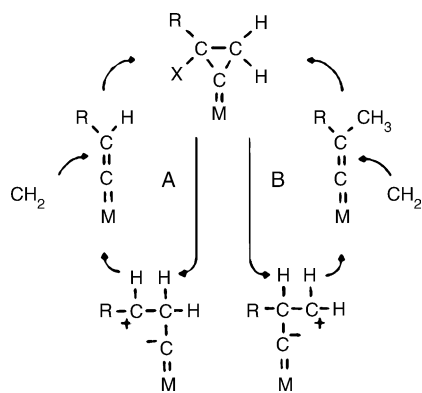


Fig. 1. Two reaction pathways for the formation of branched hydrocarbons (redrawn from Ref. [11]).

fluidized bed reactor) and found that the methyl branching increased with increasing carbon number. Anderson et al. [6] followed a procedure that was similar to Weller and Friedel but they limited growth to one end of the chain. In this simple model, there was a 90% chance that the carbon would add to the terminal position to produce a normal product and a 10% chance that the carbon would add to the penultimate carbon to produce a methyl branched product and that each chain would continue to grow. This early model was consistent with data from high-temperature FTS [5,7,8]. Weitkamp et al. [8] showed that the data from the latter three references fit a linear line when the log (wt.% straight chain isomer) was plotted against the carbon number (4–8 carbons). Anderson [9] made modifications to his original approach to calculating the fraction of branched chains and their identity to finally include three variables but the fit to experimental data did not improve materially from their initial model. McCandlish [10] proposed a mechanism that involved the insertion of CH_2 surface species into the carbon–carbon double bond of vinylidene to produce a cyclopropane intermediate (Fig. 1). The hydrogenolysis of the ring may then lead to a normal hydrocarbon or to a structure with a methyl branching (Fig. 2). Anderson [9] indicated that the McCandlish model fit the data better than his model did.

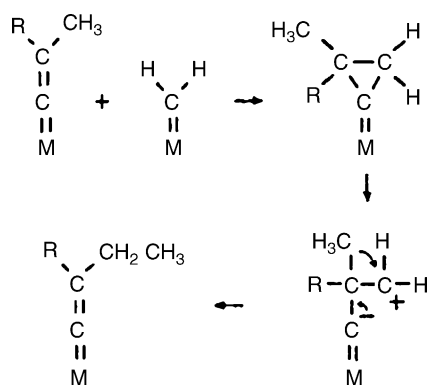


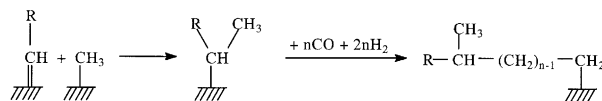
Fig. 2. Pathway for the formation of a cyclopropane intermediate and the production of branched products (redrawn from Ref. [11]).

Pichler et al. [11] showed that the primary FTS products were α -olefins and alcohols, and that chain branching increased with conversion. Schulz et al. [12,13] showed that ^{14}C -labeled propene incorporated to produce more ^{14}C -labeled branched products than ^{14}C -labeled normal products and concluded that a primary pathway for the formation of branched hydrocarbons was through the incorporation of propene into the growing chain. Lee and Anderson [14] calculated that the FTS products (from Ref. [13]) would require at least 50% incorporation of the total propene produced, and in several cases more than 100% of the total propene produced, an impossible option.

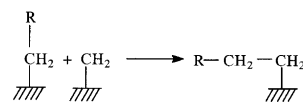
Snell [15] concluded that branched products are formed during secondary isomerization reactions. The extent of branching depends on the catalyst formulation: with low hydrogenation strength catalysts branching occurs mainly in the lighter products but with high hydrogenation strength catalysts branching occurs mainly in the heavier products. Le Roux and Dry [16] advanced the view that the reaction took place on a single site but that the chain could completely or partially separate from the surface as a free radical. Isomerization of the released primary free radical to a secondary one occurs and, when the secondary radical readsorbs it can produce methyl branched hydrocarbons. The free-radical model they developed fit the data of Bruner [5] and Weitkamp et al. [8] very well.

Schulz et al. [17–21] have recently shown that the branching probability for the species that leads to C_4 products is always low. Furthermore, the branching probability is much higher at early time-on-stream than it is at later reaction times and this dependency may vary with catalyst composition. Schulz et al. [21] considered two cases for chain branching, rejecting the option that branching was not dependent on chain length and showed that their data was consistent with branching depending upon carbon number. They show a product distribution with a peak at C_5 for branched products after which the fraction of branched products declines with increasing carbon number. The fraction of branched products exhibits an exponential decline with carbon number. They provide a mechanism for the formation of branched products according to:

Combination of methyl with alkylene:



As in analogy to linear chain growth:



Schulz and coworkers explain the time dependence of branching and its decline with carbon number as a steric effect. As the carbon chain concentration increases with time the surface becomes covered with more chains and this places

limitations on the ability to form the branched structure on the surface due to a shielding effect that increases with chain length.

In order to understand how branched alkenes and alkanes are formed, it is necessary to quantitatively measure each isomer of each carbon number. Since some GC peaks of branched alkanes co-elute with branched alkene peaks, and vice versa, it becomes necessary to use indirect means to measure the amount of each isomer. In this study, the FT products were hydrogenated or brominated, and then an accurate measurement for each branched alkanes can be made.

2. Experimental

2.1. Hydrogenation of FT products

Six grams of FTS products (oil and wax) and 0.5 g of Pt/carbon catalyst were placed in a glass hydrogenation vessel. The reaction mixture was hydrogenated under a pressure of 0.021 MPa (30 psig) at room temperature with stirring until normal alkenes were not detected in the reaction mixture. Then the reaction mixture was filtered to remove catalyst particles prior to GC and GC/MS analysis.

2.2. Bromination of FTS products

Bromine (22%) in acetic acid was added to the FTS oil or oil and wax, drop by drop with vigorous stirring, until the solution had a permanent yellow to orange color.

2.3. Analysis of FTS products

The FTS oil and the samples produced by hydrogenation and bromination were analyzed by GC and GC/MS. The branched alkanes in each carbon number were identified by GC/MS, and quantitatively determined by GC/FID.

2.4. Production of products

A 1 l continuous stirred tank reactor (CSTR) was used in this study. A sintered metal filter was installed to allow removal of wax samples from the catalyst slurry. The wax sample was extracted through the internal filter and collected in a hot trap held at 200 °C. A warm trap (100 °C) and cold trap (0 °C) were used to collect light wax and the water plus oil samples, respectively, by condensing them from the va-

por phase that was continuously withdrawn from the reactor vapor space.

CO and H₂ mass flow controllers were used to provide a simulated synthesis gas of the desired composition. After the iron catalyst was activated, syngas was introduced at a rate of 10 NL/h g-Fe. Reaction conditions were 270 °C, 1.3 MPa, H₂/CO = 0.7, and a stirrer speed of 750 rpm.

Daily gas, water, oil, light and heavy wax samples were collected and analyzed. A heavy wax sample was taken from the 200 °C hot trap connected to the filter. The vapor phase in the region above the slurry passed continuously to the warm (100 °C) and the cold (0 °C) traps located outside the reactor. The light wax and water mixture was collected daily from the warm trap and an oil plus water sample from the cold trap. Tail gas from the cold trap was analyzed with an online HP Quad Series Micro GC, providing molar compositions of C₁–C₇ olefins and paraffins as well as for H₂, CO and CO₂. Hydrogen and carbon monoxide conversions were calculated based on the gas product GC analysis results and the gas flow measured at the reactor outlet. Hydrogen, carbon monoxide and syngas conversions were calculated using the following formula (N = moles of gas):

$$\text{conversion} = 100\% \times (N_{\text{in}} - N_{\text{out}}) / N_{\text{in}} \quad (1)$$

The oil and light wax samples were mixed and separated from the water layer before analysis with an Agilent 6890 Series GC. The heavy wax was analyzed with an HP5890 Series II Plus high temperature GC while the water sample was analyzed using an HP5790 GC.

The iron catalysts were activated with CO at atmospheric pressure. Before introducing CO, the temperature of the catalyst slurry was increased to 120 °C in an inert gas; after 2 h at this temperature the inert gas was replaced with CO. The temperature was ramped at 1 °C/min to 270 °C and held at this temperature for 20 h. The temperature was then changed to the reaction temperature, the CO flow adjusted to the one used in the synthesis and the pressure was increased to reaction temperature. After the reaction pressure was reached, hydrogen flow was started and the flow was set to give the desired total flow rate and H₂/CO ratio.

The cobalt catalyst was reduced in a plug flow reactor in flowing H₂ (10% H₂ in Ar) by ramping from room temperature to 350 °C at 1 °C/min and then holding at this temperature for 8 h. The contents of the plug flow reactor were isolated from the atmosphere by valves and transported to the CSTR to which it was then connected through tubing and a valve.

Table 1
The reaction conditions and the catalyst for the Fe catalyzed FT reactions

Run ID	Bao20	Bao22	Bao26	Bao28	Bao29
Catalyst	4.6% Si, 64.6% Fe, 2.0% Cu, 1.4% K	4.6% Si, 64.6% Fe, 2.0% Cu, 1.4% K	4.6% Si, 64.6% Fe, 2.0% Cu, 1.4% K	4.6% Si, 62.2% Fe, 2.0% Cu, 5% K	100% Fe
Temp. (°C)	230	270	270	270	255
H ₂ :CO	0.67	0.67	1.70	1.70	1.91
GHSV	10	10	40	40	3.0

Table 2
The reaction conditions and the catalyst in the Co catalyzed FT reactions

Run ID	L366	L367	L368
Catalyst	10% Co/0.2% Ru/TiO ₂	15% Co/0.5% Ru/SiO ₂	15% Co/0.53% Pt/Al ₂ O ₃
Temp. (°C)	230	220	220
Pressure (psig)	350	300	275
H ₂ :CO	2	2	2
GHSV	18.3	6.73	13.4

The fixed bed reactor was overpressured with an inert gas, the valve opened, and the catalyst transferred to the CSTR, which contained 300 g of melted Polywax 3000. The catalyst was again reduced in flowing H₂ at 280 °C for 24 h. After chang-

ing to 20 °C below the reaction temperature, the pressure was increased to the reaction pressure using the flow of H₂ to be used during synthesis. CO flow was then started and the temperature increased during 2 h to the reaction temperature.

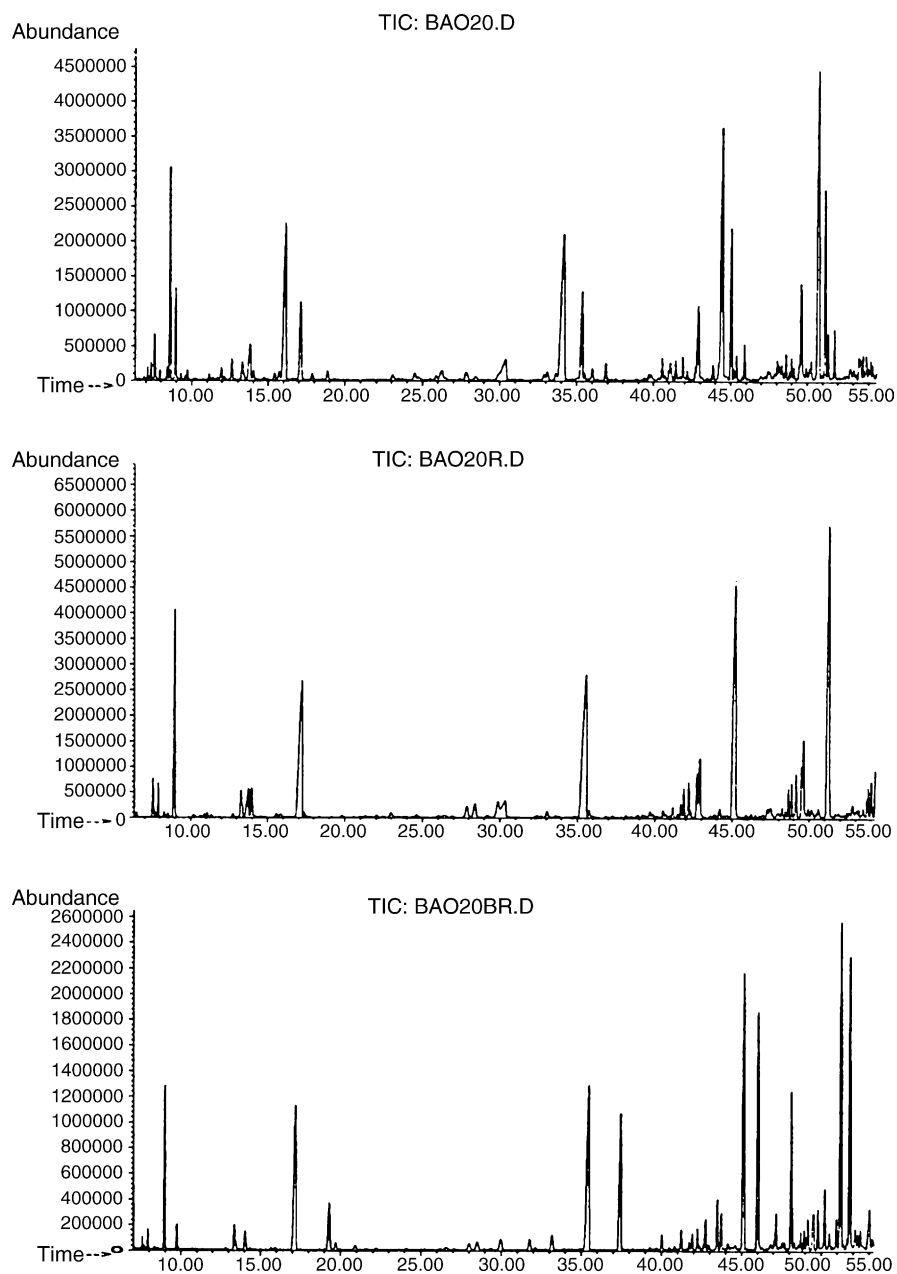


Fig. 3. A partial chromatogram of an oil sample from an iron catalyzed FTS reaction (Run ID: Bao20). Top: FTS products; middle: after hydrogenation; bottom: after bromination.

The FTS was effected at 220 °C, 1.5 MPa, H₂/CO = 2.0 and 8 NL/h/g-cat.

3. Results and discussion

Five oil samples from Fe catalyzed FTS and three oil samples from Co catalyzed FTS were hydrogenated and brominated. The FTS reaction conditions and the catalyst compositions are given in Tables 1 and 2.

All of the FTS products in the runs in this report contain 1-alkene, 2-alkenes, alkane and alcohols as well as branched hydrocarbons. After hydrogenation, the alkenes were converted to the corresponding alkane. Following bromination, the alkenes were converted to the corresponding dibromides.

Fig. 3 contains partial chromatograms of the sample from a Fe catalyzed FTS reaction (Bao20). The top chromatogram in this figure is for the FTS products; the bottom is the sample after bromination and the middle chromatogram is for the sample after hydrogenation.

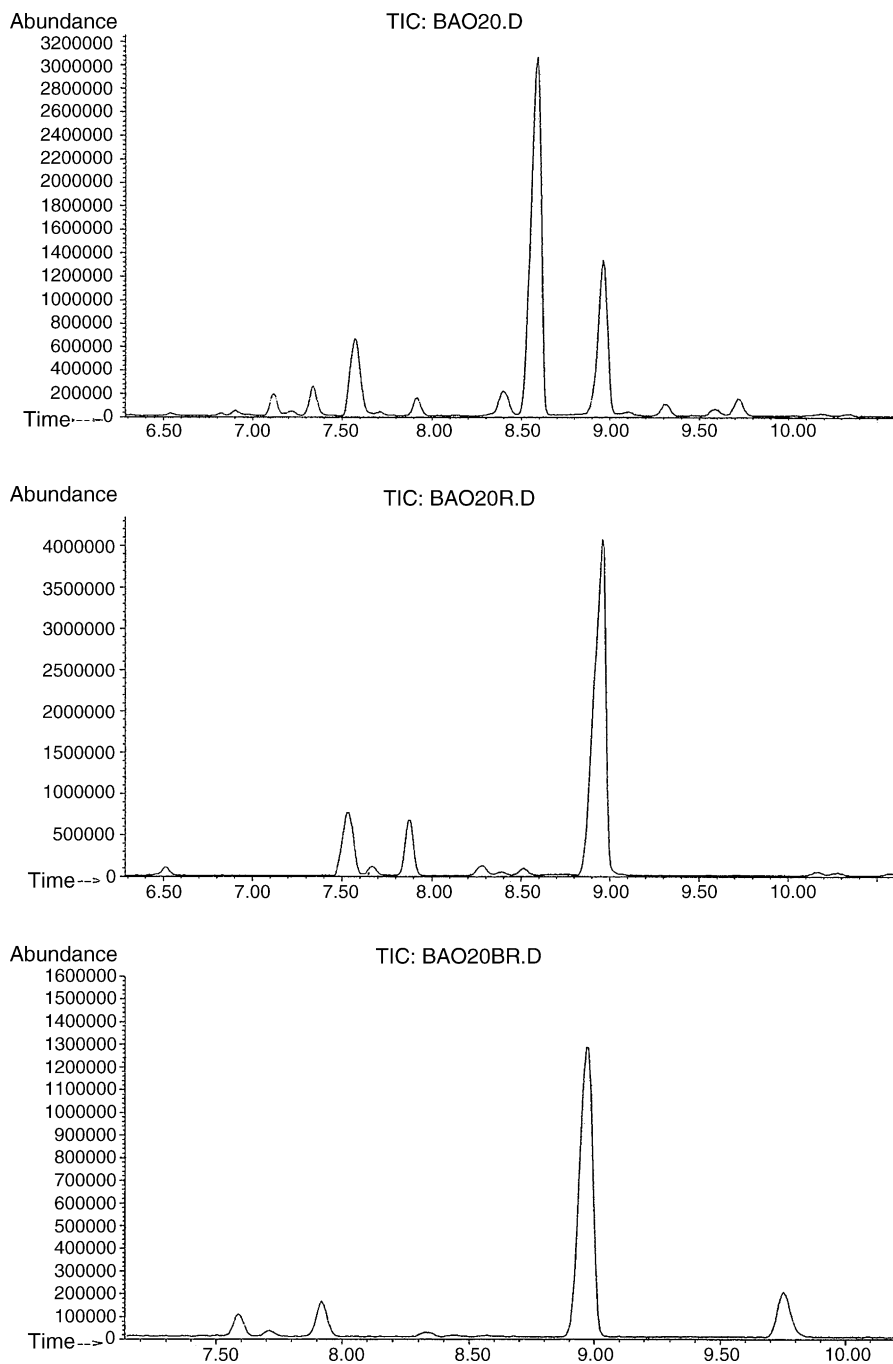


Fig. 4. A chromatogram of the C₇ fraction of Run Bao20. Top: FTS products; middle: after hydrogenation; bottom: after bromination.

Table 3
The mol% of branched alkanes in Fe catalyzed FTS products (Run ID: Bao20)

Carbon number	FTS products		After hydrogenation		After bromination	
	No. of isomers	Mol%	No. of isomers	Mol%	No. of isomers	Mol%
7	–	–	2	15.1	2	11.0
8	2	26.1	3	14.5	3	14.4
9	3	18.1	3	11.5	3	11.3
10	2	12.1	6	12.6	4	11.2
11	4	12.2	4	8.93	4	9.68
12	3	4.58	5	7.16		
13	3	7.43	5	11.6		

Table 4
The mol% of branched alkanes in Fe catalyzed FTS products (Run ID: Bao22)

Carbon number	FTS products		After hydrogenation		After bromination	
	No. of isomers	Mol%	No. of isomers	Mol%	No. of isomers	Mol%
7	2	8.82	2	16.1	2	5.10
8	3	17.7	3	19.7	3	15.9
9	3	16.6	5	19.0	3	15.3
10	4	12.7	5	19.1	4	17.3
11	4	11.9	5	20.0	4	17.3
12	4	18.9	5	15.5		
13	5	21.7	5	20.4		

Table 5
The mol% of branched alkanes in Fe catalyzed FTS products (Run ID: Bao26)

Carbon number	FTS products		After hydrogenation		After bromination	
	No. of isomers	Mol%	No. of isomers	Mol%	No. of isomers	Mol%
7	2	9.81	2	9.03	2	10.4
8	3	15.7	3	8.89	3	11.3
9	3	9.62	3	10.1	3	9.42
10	4	9.44	5	10.4	4	9.02
11	4	9.57	4	9.37	4	5.72
12	3	6.14	4	8.35		
13	4	5.89	5	9.15		

Table 6
The mol% of branched alkanes in Fe catalyzed FTS products (Run ID: Bao28)

Carbon number	FTS products		After hydrogenation		After bromination	
	No. of isomers	Mol%	No. of isomers	Mol%	No. of isomers	Mol%
7	–	–	2	14.8	2	19.2
8	2	19.7	2	25.7	3	18.0
9	3	18.5	7	20.7	3	18.0
10	3	20.9	7	20.0	3	16.4
11	4	24.8	6	19.4	4	11.7

Table 7
The mol% of branched alkanes in Fe catalyzed FTS products (Run ID: Bao29)

Carbon number	FTS products		After hydrogenation		After bromination	
	No. of isomers	Mol%	No. of isomers	Mol%	No. of isomers	Mol%
7	–	–	2	10.1	2	13.5
8	2	15.2	3	14.5	3	14.6
9	3	13.9	3	10.9	3	11.9
10	3	12.9	6	12.3	4	11.6
11	4	11.8	5	10.4	5	11.4
12	–	–	–	–	–	–
13	–	–	–	–	–	–

Fig. 4 shows the chromatogram of carbon number 7. Again, the top chromatogram is the FTS products; the middle, after hydrogenation; and the bottom, after bromination. Similar figures are obtained for the other carbon numbers and for the four Fe catalyzed FTS samples and these are not shown. After hydrogenation, the branched alkenes were converted to the corresponding branched alkanes and normal alkenes were converted to the normal alkane. The mol% of branched alkanes for each carbon number is defined as:

$$\% \text{ branched alkanes} = \frac{\text{branched alkanes}}{\text{branched alkanes} + \text{normal alkane}} \times 100 \quad (2)$$

In the case of the hydrogenated sample, the percent branched alkanes represent the total branched hydrocarbons (branched alkenes plus branched alkanes). Since it is difficult to quantitatively measure the amount of branched alkanes in the original FTS oil due to the peak overlap, bromination of the FTS oil was also carried out. The bromination of FTS oil enables us to quantitatively measure the percent branched alkanes from C₇ to C₁₁. Adding two bromines to the C₇–C₁₁ alkenes causes these bromated products to elute at times that are longer than for C₁₁ alkanes. In this case, the percent branched alkanes represents the total branched alkanes in that reaction sample. The results are given in Tables 3–7 for the Fe catalyzed FTS reactions (Bao20, Bao22, Bao26, Bao28 and Bao29, respectively). In Tables 3 through 8, the number of isomers are not the total number of possible but only the number present in sufficient quantities to be measured accurately by g.c.

Fig. 5 is a partial chromatogram of a sample from the Co catalyzed FTS (L366), and the chromatogram for carbon number 6 is shown in Fig. 6. The chromatograms of the other two Co catalyzed FTS runs (L367 and L368) are similar to Figs. 5 and 6 and are not shown. The upper curve is for the FTS products; the middle, after hydrogenation; and the bottom, after bromination. The mol% of branched alkanes for the cobalt catalysts are compiled in Table 8.

The data in Tables 3 and 4 are for runs (Runs Bao20 and Bao22) that were conducted using the same iron catalyst and the same reaction conditions except temperature (Bao20, 230 °C, Bao22, 270 °C). For the higher reaction temperature, the amounts of the branched alkanes in most of the carbon number products are higher by 5% or more.

Runs Bao22 and Bao26 (data in Tables 4 and 5) were conducted using the same catalyst and temperature but at different H₂:CO ratio and WHSV. Increasing the H₂:CO ratio from 0.67 to 1.70 and WHSV from 10 to 40 caused the amount of branched alkanes to decrease by 5–10% for each carbon number with few exceptions.

For the five Fe catalyzed FTS runs, it appears that the catalyst composition has a greater impact on the formation of branched hydrocarbons than the reaction conditions such as temperature, flow rate and H₂:CO ratio. The only difference between runs Bao26 (Table 5) and Bao28 (Table 6) is the catalyst used (for Bao26 the catalyst has Fe:K = 100:1.14 and Bao28 has Fe:K = 100:5.0); the amount of the branched alkanes increased by more than 10% for most carbon numbers as the K content increased from 1.14 to 5.0 atomic ratio.

Table 8
The mol% of branched alkanes in Co catalyzed FTS products

Carbon no.	Run no.	FT products		After hydrogenation		After bromination	
		No. of isomers	Mol%	No. of isomers	Mol%	No. of isomers	Mol%
7	L366	2	1.85	2	1.99	2	1.40
	L367	2	7.52	2	6.00	2	3.71
	L368	2	2.28	2	1.55	2	1.18
8	L366	2	2.33	2	2.45	3	1.67
	L367	3	4.69	3	4.15	3	4.05
	L368	3	2.26	3	1.57	3	1.35
9	L366	3	2.81	3	2.17	3	2.06
	L367	3	4.80	3	3.78	3	4.10
	L368	3	1.53	3	1.62	3	1.34
10	L366	3	2.19	3	2.39	3	2.08
	L367	4	4.34	4	4.05	4	4.29
	L368	3	1.51	3	1.61	3	1.37
11	L366	4	2.62	4	2.79	4	2.00
	L367	4	4.47	4	4.26	4	4.35
	L368	4	1.69	4	1.84	4	1.84
12	L366	4	1.87	5	3.02		
	L367	5	4.31	5	4.26		
	L368	4	1.60	4	1.73		
13	L366	5	3.10	5	3.34		
	L367	5	4.70	5	4.59		
	L368	5	1.84	5	1.96		
14	L366	5	3.45	5	3.72		
	L367	5	4.88	5	4.86		
	L368	–	–	–	–		

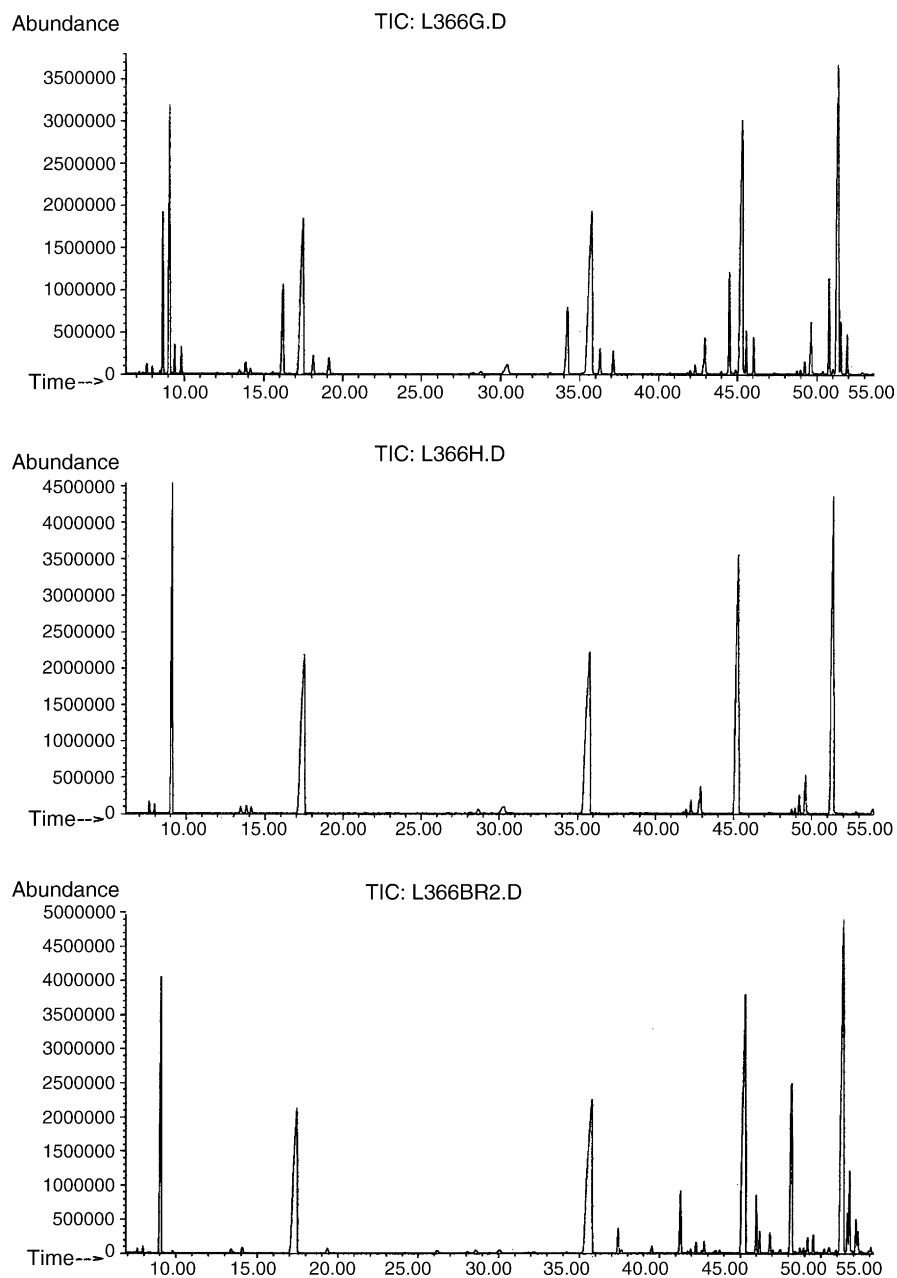


Fig. 5. A partial chromatogram of the oil sample from a Co catalyzed FTS reaction (Run ID: L366). Top: FTS products; middle: after hydrogenation; bottom: after bromination.

Run Bao29 was conducted using an unpromoted Fe catalyst (100% Fe). The amount of branched alkanes (Table 7) is lower than for runs Bao22 and Bao28. Since this run was also conducted at a higher H_2/CO ratio, intermediate temperature and low GHSV, it is difficult to tell which factor played the major role.

The major difference between the Fe and Co catalyzed FTS is that the Fe catalysts produce larger amounts of branched hydrocarbons than Co does. As shown by the data in Tables 3–8, Fe catalyzed FTS reactions produced, after hydrogenation, 10–25% of branched hydrocarbon, whereas the

Co catalyzed FTS reactions produced only 1–4% of branched hydrocarbons (Table 8).

The conditions for the three Co catalyzed FTS reactions are slightly different (Table 2) and the catalysts differ, primarily with the support. The highest percentage of branched hydrocarbons (about 4%) among these three runs with cobalt catalysts is probably due to the low WHSV, and the higher steady-state conversion produces higher iso/normal ratios.

The mol% of branched alkanes after hydrogenation is the percentage of total branched hydrocarbons (branched alkenes and branched alkanes) in the total hydrocarbon fraction.

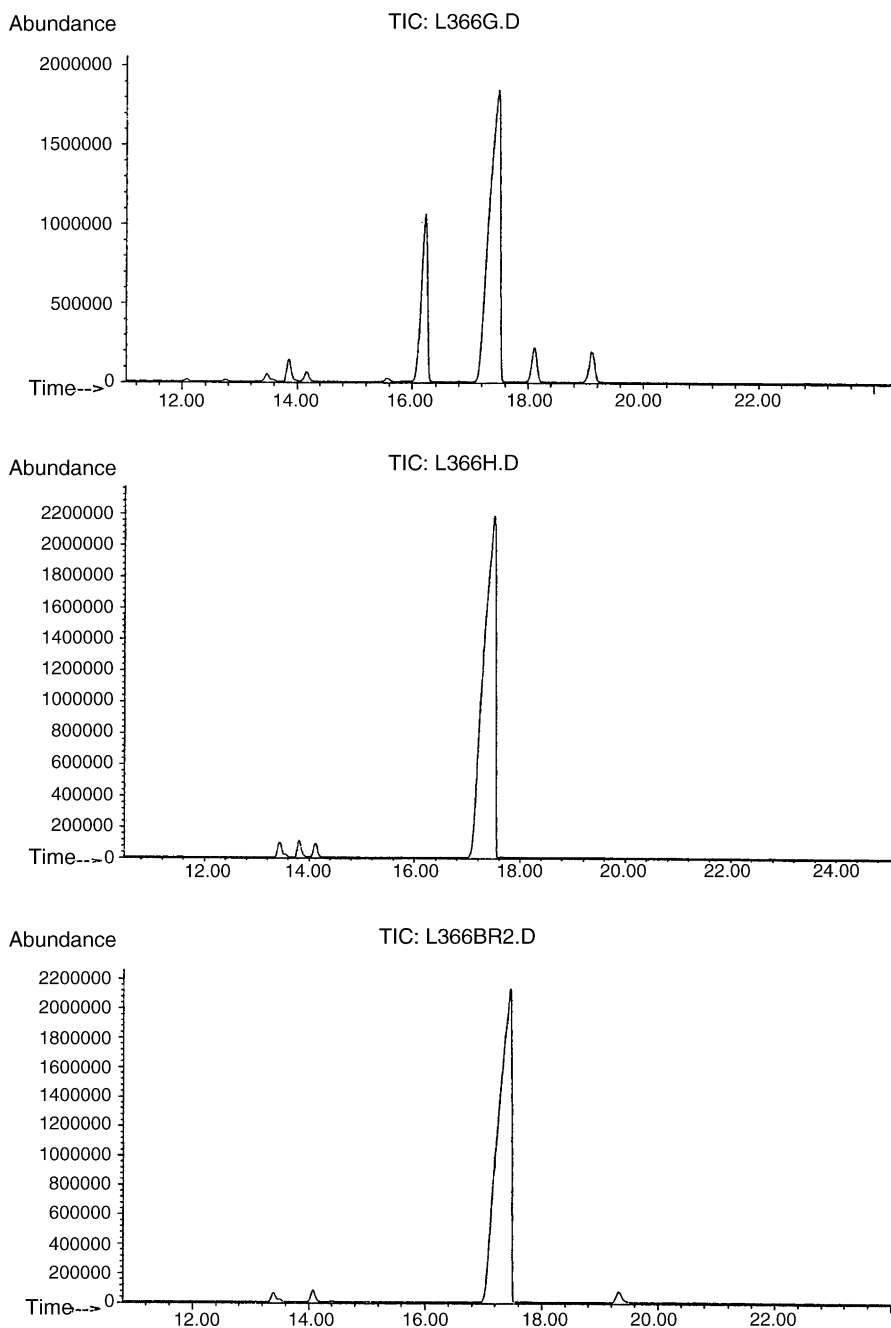


Fig. 6. A chromatogram of the C₈ fraction of Run Bao20. Top: FTS products; middle: after hydrogenation; bottom: after bromination.

Designate P_B as branched alkanes; O_B, branched alkenes; P_n, normal alkane; O_n, normal alkenes and, after hydrogenation, we have:

mol%(branched alkanes after hydrogenation)

$$= \frac{P_B + O_B}{P_B + O_B + P_n + O_n} \times 100 \quad (3)$$

The mol% of branched alkanes after the FTS reaction can be represented by the mol% of branched alkanes after bromina-

tion as shown in Eq. (4):

mol.%(branched alkanes after bromination)

$$= \frac{P_B}{P_B + P_n} \times 100 \quad (4)$$

If O_n/P_n = O_B/P_B, it can be proven that

mol.%(branched alkanes after [H])

$$= \text{mol.%(branched alkanes after [Br])} \quad (5)$$

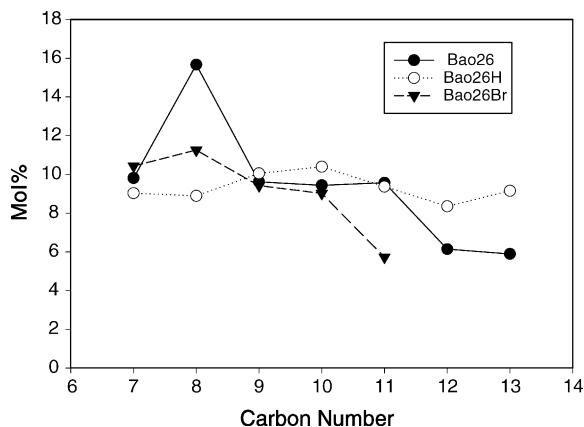


Fig. 7. The mol% of branched alkanes in the Fe catalyzed FTS products (Run ID: Bao26).

however, if $O_n/P_n < O_B/P_B$, then

$$\text{mol\%}(\text{branched alkanes after [H]}) > \text{mol\%}(\text{branched alkanes after [Br]}) \quad (6)$$

and if $O_n/P_n > O_B/P_B$, then

$$\text{mol\%}(\text{branched alkanes after [H]}) < \text{mol\%}(\text{branched alkanes after [Br]}) \quad (7)$$

For the Fe catalyzed FTS reactions, the mole percents of branched alkanes after hydrogenation in all five runs are either higher than or essentially the same as after bromination (representative data in Fig. 7). This indicates that the ratio of O_n/P_n is only slightly less than, or close to, the ratio of O_B/P_B . These results suggest that during the process of the formation of these FTS products, the rate of hydrogenation of *n*-alkenes is close to or only slightly larger than that of branched alkenes. Similar results were obtained for Co catalyzed FT reactions (representative data in Fig. 8).

The relative ratio of *n*-alkenes/*n*-alkane (O_n/P_n) can be measured accurately based on the GC. However, because of the GC peak overlap, it is very difficult to measure accurately the ratio of branched alkenes/branched alkanes (O_B/P_B). The ratio of O_B/P_B can be calculated based on the mol% of the branched alkanes (after hydrogenation and after bromination) and the ratio of O_n/P_n .

Let

$$(P_B + O_B)/(P_B + O_B + P_n + O_n) = \alpha \quad (8)$$

Table 9

The relative ratio of the products in Fe catalyzed FTS reactions (Run ID: Bao22)

Carbon number	Branched hydrocarbons/total hydrocarbons	Branched alkanes/total alkanes	<i>n</i> -Alkenes/ <i>n</i> -alkane	Branched alkenes/branched alkanes
7	0.16	0.051	2.33	1.86
8	0.20	0.16	2.00	1.96
9	0.19	0.15	1.64	1.61
10	0.19	0.17	1.48	1.47
11	0.20	0.17	1.27	1.25

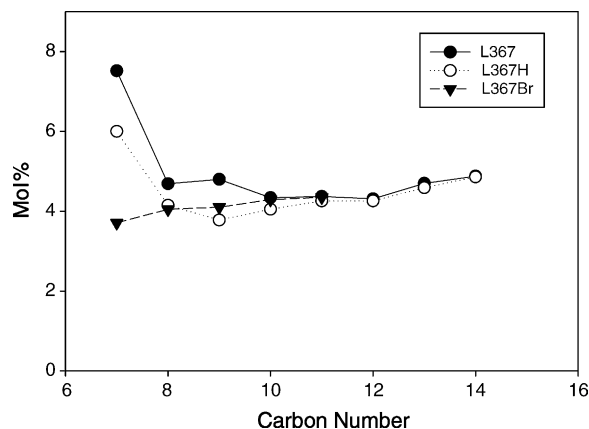


Fig. 8. The mol% of branched alkanes in the Co catalyzed FTS products (Run ID: L367).

where α is the mol% of branched alkanes after hydrogenation, and

$$P_B/(P_B + P_n) = \beta \quad (9)$$

where β is the mol% of branched alkanes after bromination. The ratio of *n*-alkenes/*n*-alkane is represented in Eq. (10):

$$O_n/P_n = \gamma \quad (10)$$

Solving Eqs. (8)–(10), we have

$$O_B/P_B = \frac{\alpha(1 - \beta)(1 + \gamma) - \beta(1 - \alpha)}{\beta(1 - \alpha)} \quad (11)$$

Based on Eq. (11), the ratio of O_B/P_B can be calculated. Also based on Eq. (11), it can be proven that if $\alpha = \beta$, then $O_B/P_B = O_n/P_n = \gamma$; if $\alpha > \beta$, then $O_B/P_B > O_n/P_n$; if $\alpha < \beta$, then $O_B/P_B < O_n/P_n$. Representative results are given in Table 9 for the Fe catalyzed FTS reactions and in Table 10 for the Co catalyzed FTS reactions.

The mol% of branched alkanes in Fe catalyzed FTS products (Fig. 9) varies from run to run. However, within a run, the different carbon number products have about the same mol% of branched alkanes. This is also true for Co catalyzed FTS reactions (Fig. 10). The major difference between Fe and Co catalyzed FTS reaction in terms of the mol% of branched alkanes is that Co catalyzed FTS reaction only produce 1–4% of branched alkanes, whereas the Fe catalyzed FTS reactions can produce as high as 20% (and probably higher) of branched alkanes.

Table 10
The relative ratio of the products in Co catalyzed FTS reactions (Run ID: L367)

Carbon number	Branched hydrocarbons/total hydrocarbons	Branched alkanes/total alkanes	<i>n</i> -Alkenes/ <i>n</i> -alkane	Branched alkenes/branched alkanes
7	0.060	0.037	0.37	0.20
8	0.042	0.041	0.30	0.29
9	0.038	0.041	0.24	0.27
10	0.041	0.043	0.20	0.22
11	0.043	0.044	0.16	0.17

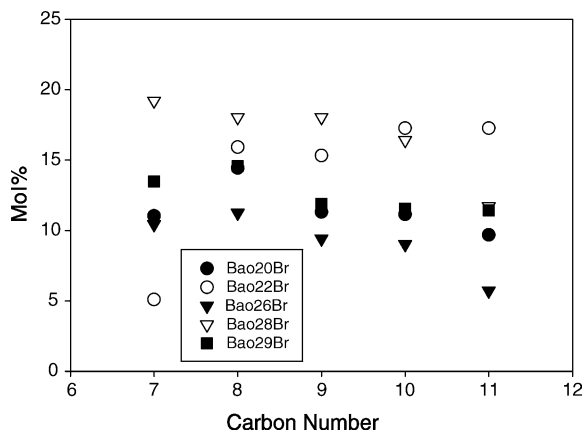


Fig. 9. The mol% of branched alkanes in the Fe catalyzed FTS products (after bromination).

One of the problems in making one model fit all of the branching data is that reaction temperature plays a significant role in defining the extent of methyl branching (Fig. 11). The high temperature data are from the circulating bed fluid catalytic reactor operated at 320 °C at Sasol (curve 4, data from Ref. [22]) and from pilot plants used for the Hydrocol plant operated in the 320–350 °C range (curve 3, data from Refs. [5] and [8]). The two curves for high temperature operations clearly show that methyl branching increases with increasing carbon number and data of this type were used for several of the earliest models. Curve 2 data are from our laboratory and are for a low alpha iron catalyst (1.4K:100Fe) operated

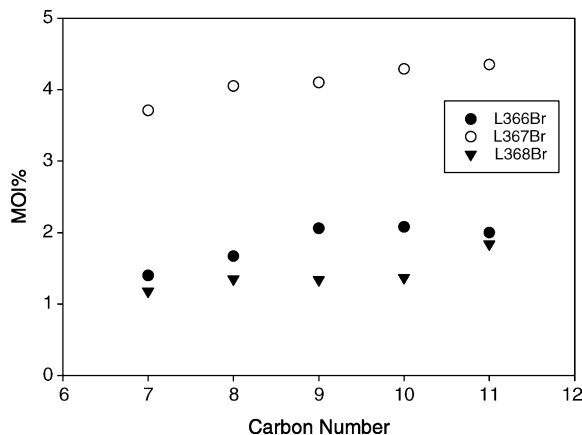


Fig. 10. The mol% of branched alkanes in the Co catalyzed FTS products (after bromination).

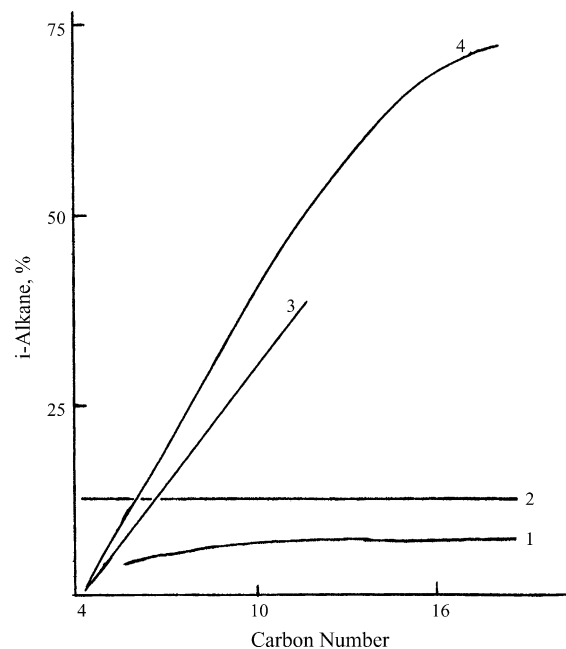


Fig. 11. Representation of the percentage of branched alkanes vs. carbon number for: 1, low-temperature cobalt catalyst; 2, low-temperature low- α iron catalyst; 3, high-temperature pilot plants to support the Hydrocol Process; 4, Sasol commercial high-temperature circulating fluid bed with iron catalyst. See text for more details.

at 270 °C. Curve 1 uses data for a cobalt-thoria-Kieselguhr catalyst operated at 190 °C and atmospheric pressure at the University of Karlsruhe [22].

For the iron catalysts used in the present study, the degrees of branching for the C₇–C₁₄ carbon numbers obtained from the samples as collected, hydrogenated and brominated are similar. This indicates that the degree of branching of the alkenes and the alkanes in the products are essentially the same. A similar conclusion can be reached for the samples obtained from cobalt supported on titania, silica and alumina catalysts. As shown by the data in Table 11, the degrees of branching for the C₄-product are very similar to those obtained for the C₇–C₁₄ carbon number fraction for both the iron and cobalt catalysts.

For the 1.44K atomic ratio catalyst, increasing the temperature for the slurry phase reaction causes only a slight change in the branching. The surface coverage is expected to be lower at the higher temperature so that, if low coverage favors the formation of more *iso*-alkanes, the change obtained in this study is opposite to that based on the prediction of Ref.

Table 11
Percentage of branching in the C₄ and C₇–C₁₄ fraction

Catalyst	C ₄ iso/normal (%)	C ₇ –C ₁₄ iso/normal (%)
1.44K:100Fe 230 °C, H ₂ /CO = 0.67	11	12
1.44K:100Fe 270 °C, H ₂ /CO = 0.67	10	17
1.44K:100Fe 270 °C, H ₂ /CO = 1.7	10	9.0
5.0K:100Fe 270 °C, H ₂ /CO = 1.7	15	18
0.0K:100Fe 270 °C, H ₂ /CO = 1.7	15	13
10% Co–0.2% Ru–TiO ₂	1.0–2.0	2.0
15% Co–0.5% Ru–SiO ₂	2.0	4.0
15% Co–0.53% Pt–Al ₂ O ₃	1.0	1.5

[17]. Based on the higher carbon number fraction, it appears that increasing the H₂/CO ratio from 0.67 to 1.7 caused a decrease in the extent of branching. Increasing the K loading from 1.44 atomic ratio to 5.0 caused an increase in the extent of branching and our data indicate that the amount of oxygenates produced also increased [23]. The unpromoted iron catalyst appears to produce a branched fraction that is as large as the lower-level K-promoted iron catalyst. All cobalt catalysts produce about one-tenth as much of the branched product as the iron catalyst, as has been observed by several earlier investigators.

The fraction identified as branched products in the FTS sample is essentially the same as the ones obtained after hydrogenation or bromination of the sample. Likewise, the fraction of branched C₄ paraffins is essentially the same as the fraction for the C₄ alkenes – this is the case for both iron and cobalt catalysts. At least two pathways could lead to this finding. In one instance, a common reaction intermediate could terminate by the addition of a hydrogen or methyl group and the fraction leading to the normal or branched product would not depend upon carbon number. In the other instance, the branched and normal products could be formed by different pathways and the contribution of these pathways does not depend on carbon number.

The cobalt catalysts produce low levels of both oxygenates and branched products whereas the iron catalysts produce much larger amounts of both oxygenates and branched products. Furthermore, for the iron catalysts, both oxygenates and branched products increase with increasing amounts of K-promoter in the catalyst. It is tempting to relate the production of the oxygenate to the branched products. One way to do this is through an aldol condensation type reaction. For this to occur, the added alkali would have to be basic enough to abstract a proton to produce an anion that would be sufficiently reactive to add to the α -olefin. There are similar reactions in the literature but the formation of the anion is usually aided by a very electron withdrawing group and it is not certain that the carboxyl group would be electron withdrawing enough to enable the formation of the anion.

Another approach for oxygenates to lead to branched hydrocarbons is through chain initiation. It has been shown that iso-alcohols lead to predominantly branched products and normal alcohols initiate chains that produce predominantly normal products [24,25]. However, the iso-alcohols initiate

chains at a lower rate than the normal alcohols. It has also been shown that for ethanol the oxygenate does not terminate chain growth [26], an argument against the addition of an anion to an alkene as described above. Thus, if chain initiation by oxygenates is the source of the branched products, the branching should be at the end of the molecule representing chain initiation and not at the end with the olefinic double bond. While there is potential to do isotopic tracer studies to learn if this is the case, the experimental work will be demanding.

4. Summary

The iso/normal alkane and alkene ratios have been found to be the same in the C₇–C₁₄ range. The olefins were converted to the alkane by hydrogenation and the iso/normal ratio of the resulting alkanes were the same as was determined for the total sample containing both alkenes and alkanes. When the olefins were converted to the dibromides, compounds which eluate at a higher retention time in g.c. and do not interfere with the C₇–C₁₄ alkane analysis, the iso/normal ratio was the same as for the total sample. Samples produced during synthesis with five iron and three cobalt catalysts showed that the iso/normal ratio was carbon number independent in the C₇–C₁₄ carbon number range. The iso/normal fraction increased with increasing potassium content for the iron catalyst. Since the oxygenates also increase with increasing potassium content, it was speculated that at least some of the iso-products may result from an aldol condensation reaction involving the oxygenate compounds. The iso/normal ratio of the C₄ products are essentially the same as for the C₇–C₁₄ products, indicating that the iso/normal ratio is the same for products up to C₁₄.

Acknowledgements

This work was supported by U.S. DOE contract number DE-FC26-98FT40308 and the Commonwealth of Kentucky.

References

- [1] U. Von Weber, *Angew. Chem.* 52 (1939) 607.
- [2] S. Weller, R.A. Friedel, *J. Chem. Phys.* 17 (1949) 801.

- [3] R.B. Anderson, Catalysis Conference of A.A.A.S. in June, 1949.
- [4] S. Weller, R.B. Anderson, *J. Chem. Phys.* 18 (1950) 157.
- [5] F.H. Bruner, *Ind. Eng. Chem.* 41 (1949) 2511.
- [6] R.B. Anderson, R.A. Friedel, H.H. Storch, *J. Chem. Phys.* 19 (1951) 313.
- [7] A. Clark, A. Anderews, H.W. Fleming, *Ind. Eng. Chem.* 41 (1949) 1527.
- [8] A.W. Weitkamp, H.S. Seelig, N.J. Bowman, W.E. Cady, *Ind Eng. Chem.* 45 (1951) 343.
- [9] R.B. Anderson, *The Fischer–Tropsch Synthesis*, Academic Press, Inc., New York, 1984, pp. 190–202.
- [10] L.E. McCandlish, *J. Catal.* 83 (1983) 362.
- [11] H. Pichler, H. Schulz, M. Elstner, *Brenst. Chem.* 48 (1967) 78.
- [12] H. Schulz, B.R. Rao, M. Elstner, *Erdöl-Kohle-Erdgas-Petrochem.* 23 (1970) 651.
- [13] H. Pichler, Schulz, *Chem. -Ing. -Tech.* 42 (1970) 1162.
- [14] C.B. Lee, R.B. Anderson, *Proceedings of the Eighth Intern. Congr. Catal.*, 1984.
- [15] R. Snell, *J. Mol. Catal.* 50 (1989) 103.
- [16] J.H. Le Roux, L.J. Dry, *J. Appl. Chem. Biotechnol.* 22 (1972) 719.
- [17] H. Schulz, Z. Nie, F. Ousmanov, *Catal. Today* 71 (2002) 351.
- [18] H. Schulz, G. Schaub, M. Claeys, T. Riedel, *Appl. Catal. A: Gen.* 186 (1999) 215.
- [19] H. Schulz, Z. Nie, in: A. Corma, F.V. Melo, S. Mendioroz, J.L.G. Fierro (Eds.), *Studies in Surface Science and Catalysis*, 120, Elsevier, Amsterdam, 2000, p. 1145.
- [20] H. Schulz, E. Van Steen, M. Claeys, *Stud. Surf. Sci. Catal.* 81 (1994) 455–460 (Natural Gas Conversion II).
- [21] H. Schulz, K. Beck, E. Erich, in: M.J. Phillips, M. Ternan (Eds.), *Proceedings of the Ninth Int. Congr. Catal.*, Canada, The Chem. Inst. vol. 2 (1988) 829–836.
- [22] H. Pichler, H. Schulz, D. Kühne, *Brennstoff-chem.* 49 (1968) 344.
- [23] L. Xu, S. Bao, D.J. Houpt, S.H. Lambert, B.H. Davis, *Catal. Today* 36 (1997) 347.
- [24] L.-M. Tau, H.A. Dabagh, B.H. Davis, *Energy Fuels* 5 (1991) 174.
- [25] A. Raje, B.H. Davis, in: J.J. Spring (Ed.), *Catal. Royal Soc. Chem.* 12 (1996) 52–131 (Cambridge).
- [26] B. Shi, B.H. Davis, *Topics Catal.* 26 (2003) 157.