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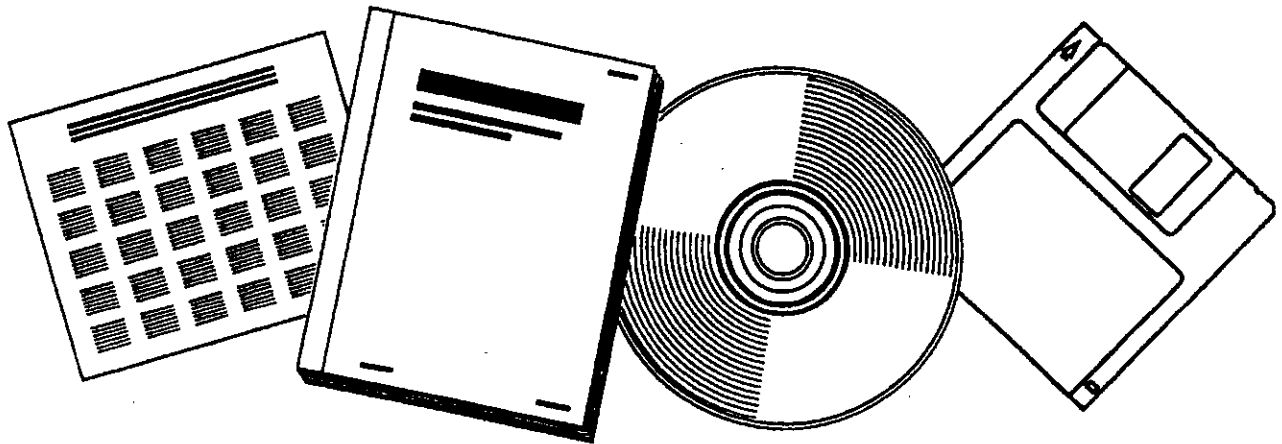
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FISCHER-TROPSCH SLURRY PHASE PROCESS VARIATIONS: QUARTERLY REPORT FOR PERIOD JANUARY 1, 1987 TO MARCH 31, 1987

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Fischer-Tropsch Slurry Phase
Process Variations

Quarterly Report for Period
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Summary

The results of a detailed series of studies are reported herewith on the effects of adding ethanol during Fischer-Tropsch synthesis on a reduced fused magnetite catalyst at 248°C and 9.2 atm. Ethanol decreased the hydrogenation capabilities of the catalyst as reflected in lower CH₄ formation and higher olefin-paraffin ratio of the products. The value of α (C₃-C₇) based on hydrocarbons was unaffected, but increased quantities of acetaldehyde, C₃ oxygenates and ethyl acetate were found.

We found no evidence for significant ethanol incorporation into growing chains. This is consistent with previous studies by Kummer et al. (1951) and Kokes et al. (1957) with radioactively-labelled ethanol. In their work, incorporation into growing chains decreased markedly with increasing pressure and less occurred over a doubly promoted iron catalyst (MgO, K₂O) than over a singly promoted catalyst (ThO₂). The catalyst here was triply promoted (Al₂O₃, K₂O, CaO).

Reactions of Ethanol Added During
the Fischer-Tropsch Synthesis

Introduction

In the Fischer-Tropsch synthesis, in addition to paraffins, 1-olefins and 1-alcohols are significant primary products. Once formed, these latter can undergo secondary reactions such as hydrogenation, isomerization, and incorporation into growing chains. The objective of this task is to study such secondary reactions of selected primary products by adding the compound of interest to the synthesis gas feedstream or directly to the reactor under normal Fischer-Tropsch synthesis conditions. The compounds to be studied are ethanol, ethylene, 1-butene, 1-decene ($C_{10}H_{20}$) and 1-eicosene ($C_{20}H_{40}$). In the primary synthesis ethanol is the dominant alcohol and C_2 species appear to be unusually reactive in secondary processes. The other olefins are to be studied to see if any regularities are found with increasing molecular weight of this homologous series.

Experimental Procedure

In general, experiments with and without each additive are conducted at 248°C, pressures in the range of 7.8 to 14.8 atm, at high and low CO conversions, and with high and low concentrations of the additive in the feed. CO conversion is varied by changing the flow rate of synthesis gas to the reactor.

With a fresh catalyst at least 40 hours are first allowed to elapse to insure that steady state activity has been achieved. A material balance is then run without additive addition for about

6 hours to establish a base case. The additive is then introduced continuously for some 4 to 10 hours after which steady state is essentially achieved and a material balance is then obtained over a 6-7 hour period.

Results and Discussion - Ethanol

The conditions for all of the experiments are summarized in Table 1 together with the resulting CO and H₂ conversions and the resulting partial pressures of the feed additive in the exit gas of the reactor. In all cases the addition of ethanol significantly increased the partial pressure of the additive in the reactor over that which existed during normal Fischer-Tropsch synthesis.

Results

The conversion of the ethanol in the feed was calculated by first subtracting the flowrate of ethanol leaving the reactor for the experiments with no feed addition (base case) from the flowrate of ethanol leaving the reactor for the feed addition experiments conducted at the same conditions. Together with the value of the ethanol flowrate into the reactor, the conversion and rate of consumption of the ethanol in the feed could be calculated. At high CO conversion, the averaged conversion of ethanol in the feed was about 30%, while for the single experiment conducted at low CO conversion, the conversion of the ethanol in the feed was less than 1%.

The addition of ethanol to the feed did not significantly affect the CO or H₂ conversions at low CO conversions (see Table

2). At high CO conversions, the ethanol addition did result in a significant decrease in H₂ conversion but only a slight decrease in CO conversion. For example, for experiment 29,6 (= Run Fe 29, Experiment #6) at ethanol partial pressure of 0.02 atm, $x_{H_2} = 0.68$ and $x_{CO} = 0.93$, while for experiment 29,7 at ethanol partial pressure of 0.46 atm, $x_{H_2} = 0.59$ and $x_{CO} = 0.89$.

Shown in Table 1 are the pertinent selectivity results from these experiments. At both high and low CO conversions, the increased partial pressure of ethanol in the reactor resulted in a significant decrease in methane selectivity, and an increase in the olefin/paraffin and α -olefin/ β -olefin ratios. The latter two ratios were more affected by ethanol at high CO conversions. The selectivity to form ethylene significantly increased, especially at high CO conversions. However, the selectivity to form ethane decreased by approximately an equal amount, as reflected by the essentially constant overall selectivity to form ethylene plus ethane.

The selectivity to form C₃ hydrocarbons (propane and propene) remained essentially constant, but there was an increased selectivity to form ethanal (acetaldehyde), C₃ oxygenates, and ethylacetate. The latter compound was positively identified (Cambridge Analytical Associates, Inc.) using g.c. mass spectrometer analysis and further confirmed in our laboratories using ethylacetate as a spike in the g.c. samples. The C₃ oxygenates could not be accurately separated quantitatively into propanol and propanone, but careful analysis

of the samples containing the C₃ oxygenates revealed that an increase in the propanone selectivity was responsible for the observed increase in the overall C₃ oxygenate selectivity. By a material balance most of the ethanol disappearance could be accounted for by appearance of acetaldehyde, C₃ oxygenates and ethyl acetate.

In Figure 1 is shown the effect of ethanol addition at a high CO conversion on the C₁-C₇ product distribution for experiments 29,6 and 29,7. This is normalized without the C₂ fraction. The methane selectivity dropped, but the chain growth probability as characterized by α was not significantly affected. Ethanol addition had no significant effect on the amount of CO₂ formed per mol of CO consumed, i.e., it did not affect the water gas shift.

Discussion

Added ethanol did not significantly affect the conversion of CO, suggesting either weak adsorption of the ethanol relative to CO or adsorption of the ethanol on sites other than those active for CO adsorption. A similar lack of synthesis inhibition by ethanol was also observed by Kokes et al. (1957). In that study, synthesis gas (H₂/CO = 1) containing radioactive ethanol (1.5 vol%) was passed over a reduced "singly promoted" iron catalyst (0.64% Al₂O₃ and 2.00% ZrO₂) at 239° C and 1 atm, and over a reduced "doubly promoted" iron catalyst (4.6% MgO, 0.6% K₂O, 0.6% SiO₂, and 0.6% Cr₂O₃) at 241-275°C and 1-21.5 atm. For both catalysts the ethanol addition did not retard the synthesis.

In a similar study by Kummer et al. (1951) when synthesis

gas ($H_2/CO = 1$) was passed over a reduced singly promoted iron catalyst (1.55% Al_2O_3 and 0.58% ZrO_2) at about 230° C and 1 atm, the addition of radioactive ethanol (1.6 vol%) reportedly retarded the synthesis. However, catalytic activity was characterized by gas contraction, rather than CO conversion. Here, while the CO conversion remained constant, the H_2 conversion decreased upon ethanol addition, thus decreasing the overall contraction.

It is apparent that the added ethanol decreased the hydrogenating characteristics of the catalyst, as reflected in the decrease in methane selectivity and the increase in C_2 - C_4 olefin/paraffin ratios. The increase in the olefin/paraffin ratios also suggests that the ethanol is competitively adsorbing with the α -olefins for active sites, thus inhibiting the secondary reactions of the α -olefins. This is supported by the observation that the α -olefin/ β -olefin ratios also increased with increasing ethanol partial pressure. Kummer et al. (1951) also noted this decrease in the hydrogenating activity of the catalyst with added ethanol as evidenced by the increase in the C_2 , C_3 and C_4 olefin/paraffin ratios.

The decrease in methane selectivity cannot be attributed to the reaction of adsorbed ethanol with adsorbed methane precursors. Such a reaction should result in an increased selectivity to form C_3 hydrocarbons, but this was not found. The increase in the C_2 olefin/paraffin ratio is not the result of an increased formation of ethylene due to ethanol dehydration, since then the total C_2 hydrocarbon selectivity, ethylene + ethane,

should increase with added ethanol. Once again, this was not observed. *

All of the above effects were more predominant at the higher CO conversions. At the correspondingly lower CO partial pressures, more sites are available for the ethanol to adsorb and interact with the ongoing synthesis.

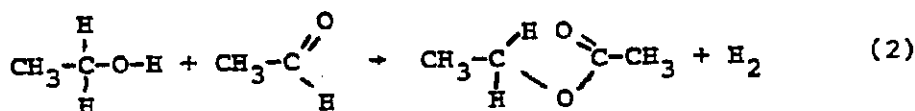
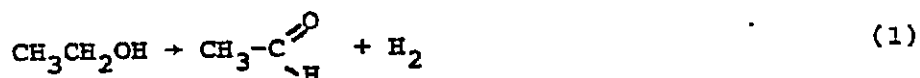
Ethanol did not significantly incorporate into growing hydrocarbon chains to form higher hydrocarbons, as evidenced by the lack of increase in the C₃ hydrocarbon (i.e., propane + propylene) selectivity with added ethanol. In contrast in the study of Kummer et al. (1951) at atmospheric pressure, about 35% of the radioactive ethanol added was incorporated and the resulting hydrocarbon products (up to C₁₀) had approximately a constant radioactivity per mole, suggesting that ethanol could act as a chain initiator. It was further shown that the chain initiation occurred preferentially at the methylene carbon atom

Kokes et al. (1957) extended the work of Kummer et al. by radioactive tracer experiments with a doubly promoted catalyst at varying pressure and temperatures (239-275° C). The percent incorporation of the ethanol was not a function of temperature or contraction, but fell from 18% to 7% to 2.2% as the pressure was increased from 1 to 7.5 to 21 atm. They also concluded by comparison to the results of Kummer et al. that less incorporation occurred over a doubly promoted catalyst (MgO, K₂O) than over a singly promoted catalyst (ThO₂).

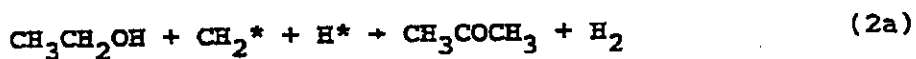
The lack of evidence for significant ethanol incorporation

in this study is consistent with the conclusions of Kokes, et al. since the experiments here were at relatively high pressures (9.2) over a triply promoted catalyst (Al_2O_3 , K_2O , CaO). A small degree of incorporation could not have been detected here.

The observed increases in selectivity to form both acetaldehyde and ethylacetate with an increase in ethanol partial pressure are probably interrelated. The acetaldehyde is probably produced by dehydrogenation of the ethanol (Reaction 1) and the ethylacetate by the subsequent reaction of the acetaldehyde with ethanol (Reaction 2).



The observed increase in selectivity to form propanone (acetone) with an increase in ethanol partial pressure suggests that the ethanol is possibly reacting with surface methylene species by a reaction such as 2a:



The fact that propanone formed in Reaction 2a instead of 1-propanol further suggests that the ethanol is bounded to the catalyst surface at the oxygenated carbon. The hydrogen produced via Reactions 1, 2 and 2a could account for less than 10% of the observed decrease in hydrogen conversion. This decrease thus reflected rather a decrease in the activity of the hydrogenation functionality of the catalyst.

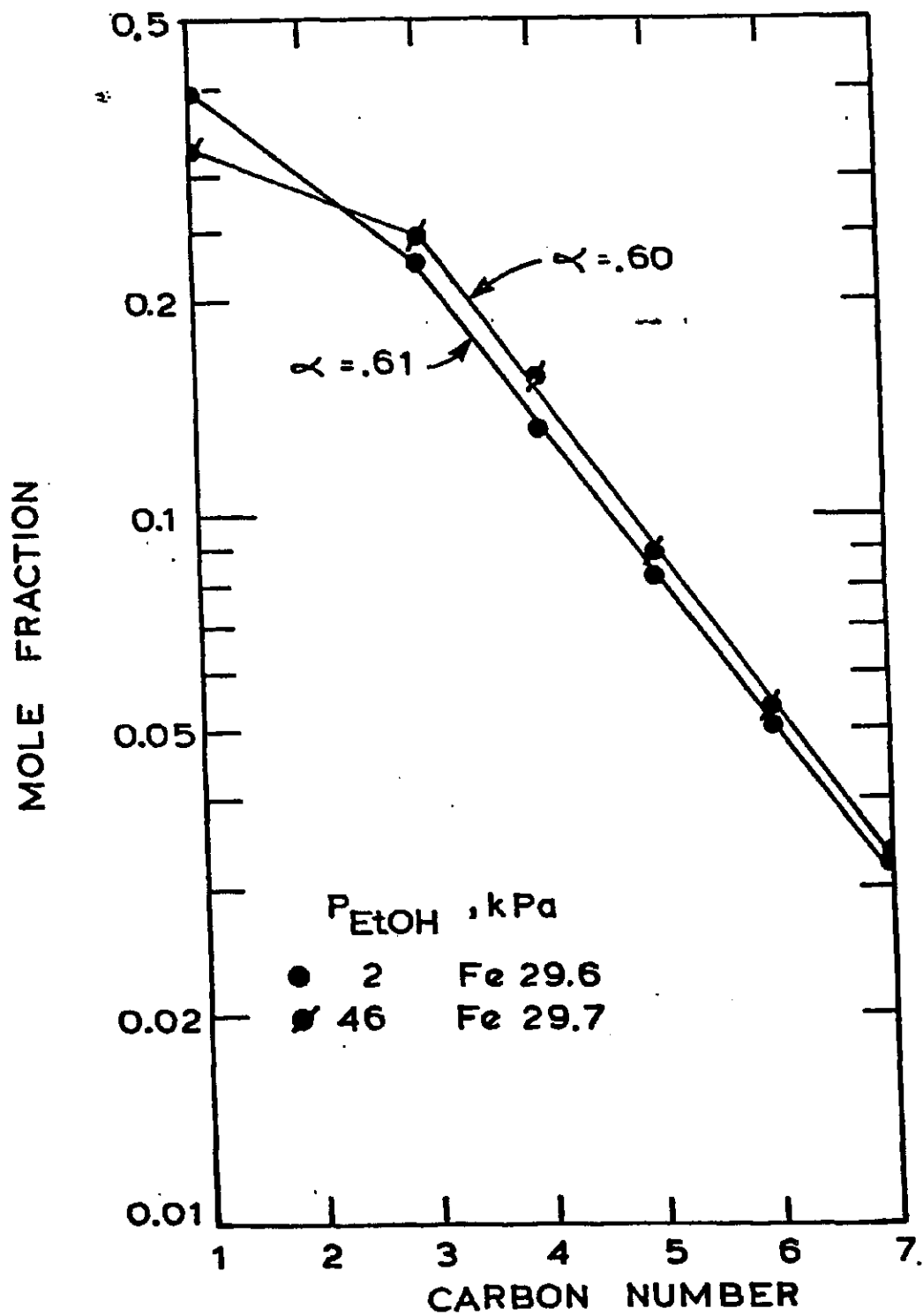


Table 1 - Selectivity results from ethanol feed addition experiments
(248°C, 9.2 atm, 0.90-0.94 H₂/CO).

Run #	High CO Conversion					Low CO Conversion	
	24	24	24	29	29	24	24
Experiment#	29	31	30	6	7	32	33
CO Conversion (%)	89	89	88	93	89	40	42
P _{H₂} (atm)	2.98	3.10	3.07	2.80	2.99	4.07	3.95
P _{CO} (atm)	0.97	0.93	0.90	0.67	0.86	3.67	3.46
P _{CO₂} (atm)	3.85	3.53	3.13	4.02	3.42	1.10	1.13
P _{H₂O} (atm)	0.26	0.36	0.59	0.35	0.34	0.12	0.09
P _{EtOH} (atm)	0.02	0.35	0.58	0.02	0.46	0.01	0.33
Vol. % EtOH in Feed	--	3.1	6.4	--	4.0	--	2.9
Conversion of EtOH in feed (%)	--	29	38	--	28	--	1.0
<u>Moles Product per Mole CO Consumed (x 100)</u>							
Methane	5.5	3.7	3.5	5.0	4.2	3.1	2.6
Ethylene	0.37	0.78	1.00	0.6	1.5	0.97	1.08
Ethane	2.0	1.5	1.3	1.9	1.3	0.54	0.43
Ethylene + Ethane	2.4	2.2	2.3	2.5	2.8	1.5	1.5
Propylene + Propane	2.6	2.3	2.3	2.7	2.8	1.4	1.3
Ethanal (Acetaldehyde)	0.01	0.18	0.35	0.01	0.10	0.04	0.36
Ethylacetate	0.00	0.17	0.30	0.00	0.29	0.00	0.02
Propanal + Propanone	0.03	0.17	0.25	0.08	0.28	0.03	0.11
CO ₂	46.9	46.8	46.4	47.1	49.3	45.1	44.4
Olefin/Paraffin							
C ₂	0.19	0.52	0.77	0.33	1.15	1.8	2.5
C ₃	1.9	4.0	4.7	3.4	6.7	4.6	4.8
C ₄	2.6	4.0	4.6	3.7	6.0	4.0	4.2
α-Olefin/β-Olefin							
C ₄	1.7	5.3	8.0	2.8	13.4	17.0	28.0
C ₅	1.7	5.7	9.0	2.7	12.9	20.0	35.0

Table 2 - Experimental Results¹ (248°C, (H₂/CO) feed = 0.90 - 0.97)
 Before/During Feed Addition

Additive	Run #	Experiment #	P _{TOT} (atm)	X _{CO} (%)	X _{H₂} (%)	Partial Pressure Of Additive in Exit Gas (atm)
Ethanol	Fe24	32/33	9.2	40/42	26/27	0.01/0.33
	Fe24	29/30,31	9.2	89/89, 88	65/59, 56	0.02/0.35, 0.58
	Fe29	6/7	9.2	93/89	68/59	0.02/0.46

¹Numbers separated by /'s in the table represent "base case run"/"feed addition run". Numbers separated by commas indicate several experiments wherein the concentration of the additive in the feed was varied at set synthesis conditions.