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NOVEL APPROACHES TO THE PRODUCTION OF HIGHER
ALCOHOLS FROM SYNTHESIS GAS

Quarterly Technical Progress Report No. 13

For The Period October 1, 1993 to December 31, 1993

Contractor

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July 6, 1994

Prepared for the United States Department of Energy
Under Contract No. DE-AC22-90PC90043
Contract Period 25 September 1990 - 31 December, 1994

QTECH013

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NOVEL APPROACHES TO THE PRODUCTION OF HIGHER ALCOHOLS FROM SYNTHESIS GAS

Quarterly Technical Progress Report
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CONTRACT OBJECTIVES

- Task 1. Program Management.
- Task 2. Liquid-Phase, Higher Alcohol Process with Recycle of Lower Alcohols.
- Task 3. Novel Catalysts for Synthesis of Higher Alcohols.
- Task 4. Synthesis of Higher Alcohols via Acid-Base Catalysis.
- Task 5. Technology Evaluation.

Summary of Activity

In Task 2,

- The mass balances from the September, 1993 methanol synthesis run closed to within $\pm 5\%$, indicating that the analytical techniques and measurement procedures that have been developed to date are accurate and reliable. However, methanol production was severely depressed due to catalyst poisoning, probably by metal carbonyls. Thermodynamic calculations show that the current carbonyl traps are not suitable for methanol synthesis service.
- X-ray photoelectron spectroscopy analysis showed essentially no carbon on the poisoned catalyst from the September, 1993 methanol synthesis run, as compared with the high carbon levels on the spent catalyst from the April, 1993 methanol synthesis run.

- Experiments showed that oil foaming can occur at ambient temperatures. New procedures for initial reactor pressurization/depressurization have been developed.
- Infrared spectroscopy of boiled mineral oils showed the presence of unsaturated carbon chains. The extent of unsaturation is not yet known.
- A test of a new overhead system on the stirred autoclave reactor showed a marked improvement in oil retention within the reactor.

Technical Details

A. September, 1993 Methanol Synthesis Run and Methanol Synthesis Catalyst Poisoning

Another series of methanol verification tests was conducted with methanol synthesis, as shown in Table 1. During the seventh day of continuous operation, operation was terminated prematurely during the third set of process conditions due to pluggage problems in the reactor carbonyl trap.

Table 1
Process Conditions for the Methanol Verification Runs

Run	Pressure (psig)	Reactor Temp. (°C)	GHSV (sl/kg cat - hr)
1	750	250	5000
2	750	250	10000
3	2500	250	16500

The first two sets of process conditions (Runs 1 and 2) were completed without incident. As shown in Table 2, the elemental material balances from these runs closed within $\pm 5\%$, except for one case. This confirms that the analytical methods and measurement procedures are accurate and reliable. In Table 2, the elemental deviation is defined as:

$$\% \text{ Deviation} = \frac{\text{Elemental Mass In} - \text{Elemental Mass Out}}{\text{Elemental Mass In}} \times 100$$

Therefore, positive values indicate that input is greater than output, and vice versa for negative values.

Table 2
Elemental Material Balance Deviations for
September 1993 Methanol Synthesis Runs

Run	Mass Balance	% Elemental Deviation		
		H	C	O
1	1	-0.27	3.74	6.84
	2	0.61	-3.43	-2.70
	3	1.53	-0.78	1.23
	4	1.12	-1.52	0.19
	5	0.23	-3.49	-3.05
2	1	1.20	-2.91	-2.59
	2	1.47	-1.15	-0.53
	3	1.26	-2.23	-2.20
	4	2.49	-2.62	-3.83
	5	1.25	-1.92	-1.46

These material balances are based on gas standard analyses carried out by the Research Triangle Institute (RTI). The original gas standard analyses from National Welders Specialty Gases (NWSG) were suspect due to inconsistencies in the mass balances. NWSG re-analyzed the standards and reported the same results as they originally supplied. However, the RTI analyses were further supported in this laboratory by experiments in which the gas chromatograph (GC) sample pressure was varied with pure gases to simulate different concentrations of the gas in the GC sample loop. Figure 1 illustrates the significant difference for the hydrogen gas standard results. The carbon monoxide and carbon dioxide results did not differ significantly between the three analyses (RTI, NWSG and pressure variation). A new set of gas standards will be ordered from another gas supplier.

Despite the excellent closure of the material balances, the initial rate of methanol formation was much lower than expected, and it decreased as the runs continued. Figure 2 shows the overall rate of methanol formation per unit weight of catalyst, commonly referred to as catalyst productivity, versus time.

Figure 1
Hydrogen Gas Standards

Figure 2
Catalyst Productivity for the September, 1993
Methanol Synthesis Runs

About 15 hrs into the first methanol synthesis run (Run #1) the catalyst productivity was only 1.62 mol/kg-hr. Typical catalyst productivity for methanol synthesis under these process conditions is 17 mol/kg-hr (Roberts, et al., 1990).

This behavior indicates severe catalyst deactivation, even at the beginning of the run, probably caused by catalyst poisoning. Thermal deactivation is also possible, but catalyst life tests performed at these conditions by Roberts, et al. (1990) indicated only about a 10% loss in catalyst productivity by this mechanism during 800 hours of operation. Also, Inductive Coupled Plasma (ICP) analysis of the spent catalyst from the September, 1993 run showed 980 ppm iron and 527 ppm nickel in the catalyst bulk, as compared to 34 ppm Fe and 56 ppm Ni in fresh, unused catalyst. This result further suggests catalyst poisoning, probably caused by metal deposition from metal carbonyls.

A result of metal carbonyl deposition on the catalyst is methane formation during the synthesis run. The deposited metal can behave as a methanation catalyst in the reactor, giving rise to methane in the reactor outlet stream. Figure 3 illustrates the change in product yield from methanol to methane during the course of the series of runs, again indicating catalyst poisoning due to metal deposition. For methanol and methane, the results are expressed as the fractional yield of product *i* based on moles of carbon converted, $Y(i/MCC)$, defined as:

$$Y\left(\frac{i}{MCC}\right) = \frac{(\text{atoms of C})}{(\text{molecule of } i)} \times \frac{(\text{moles of } i \text{ out} - \text{moles } i \text{ in})}{(MCC)}$$

where MCC is defined as the total moles of carbon actually converted to product. This fractional yield is also referred to as the carbon efficiency in the literature.

Roberts, et al. (1993) carefully evaluated Cu/ZnO methanol synthesis catalyst deactivation by both thermal sintering and metal poisoning. A model was developed to describe the catalyst deactivation based upon concentration of metal poisons on the catalyst. Therefore, a comparison of the predictions of that model with the results of the September 1993 methanol synthesis run is warranted. The catalyst poisoning model is based on reduced rate constants, so rate constants were determined from the experimental values of catalyst productivity, r_M , using the rate equation

Figure 3
Product Yields for the September, 1993
Methanol Synthesis Runs

$$r_M = k'(p_{CO})^{1/3}(p_{H_2})^{2/3}\{1 - (p_M/p_{CO}/p_{H_2}^2 K_{eq})\}$$

Roberts' model separated thermal deactivation from poisoning by determining $k^*(t)$, which is the rate constant that would have existed at the same time as $k'(t)$ if the feed had been poison-free. A reduced rate constant was then calculated as $k'(t)/k^*(t)$. However, for the September, 1993 methanol synthesis tests, the total time on-stream was less than 150 hours. As discussed previously, thermal deactivation effects are minimal for this short operating time. Therefore, instead of determining a $k^*(t)$ for each $k'(t)$; the rate constant at time zero, $k'(0)$, was used to calculate $k^*(t)$. This assumes that at time zero no catalyst poisoning or thermal deactivation has occurred. The value of $k'(0)$ is determined by plotting the rate constants versus time and determining the y-intercept, as shown in Figure 4.

As shown in Figure 4, the value of $k'(0)$, the y-intercept, is 0.075 mol MeOH/kg-hr-atm. Since the only values of Ni and Fe concentrations on the catalyst were measured after the runs were terminated, then the value of $k'(135.5 \text{ hours})$ is the only value with any significance with respect to the poisoning comparison. Therefore, the reduced rate constant, $k'(135.5)/k'(0)$ is about 0.25.

The Roberts' deactivation model specifically relates the reduced rate constant $k'(t)/k^*(t)$ with the concentrations of iron and nickel on the surface of the catalyst, i.e.,

$$k'(t)/k^*(t) = 1 - \alpha_{Fe}C_{Fe} - \alpha_{Ni}C_{Ni}$$

where the α 's are the effective amount of catalyst surface area poisoned per unit of metal on the surface, and the C's are the surface concentrations of the metals. For comparison with the results of the September, 1993 runs, the approximate values of α determined by Roberts, et al. were used. Also, the BET surface area of reduced catalyst which has not been exposed to CO was used to determine metal poison coverage. Finally, all of the Fe and Ni concentrations as reported by ICP analysis were assumed to be located on the surface. Given these assumptions, the predicted value of the reduced rate constant, $k'(135.5)/k^*(135.5)$, based on Roberts' deactivation model, is -0.07 as compared to 0.25 derived from Figure 4. Supporting calculations are provided in Appendix C. A negative value of the reduced rate constant is physically

Figure 4
Rate Constants for the September, 1993
Methanol Synthesis Runs

impossible. The calculations based on Roberts' model indicate that enough Fe and Ni had deposited to essentially totally deactivate the catalyst.

This comparison must be qualified in several respects. First, the September, 1993 tests operated for an additional 8 hours under the conditions of Run #3, high pressure and high space velocity, beyond the time that the last value of k' was measured. As will be shown later, possibly 90% of the iron and nickel was deposited during this time. Therefore, the actual values of Fe and Ni on the catalyst surface 135.5 hours into the run could have been substantially lower than those used for the model calculation. If so, the resulting reduced rate constant would increase.

Second, the ICP analyses of the catalyst samples often do not total to 100%, even when oxygen is taken into account. Therefore, the numbers were normalized, which typically raises the values of the metal concentrations. If the original "raw" data for the catalyst samples are used, then a reduced rate constant, $k'(135.5)/k^*(135.5)$, of 0.66 is calculated from the model. Obviously, uncertainty in ICP analyses can account for substantial error.

Third, the BET surface area of the catalyst at 135.5 hours was not directly measured. Since the catalyst probably did not experience significant thermal deactivation, a surface area measurement by Air Products of reduced BASF S3-86 catalyst was used as an estimate. The surface area is used directly to calculate the surface metal concentrations, so any change in area could significantly change the calculated reduced rate constant.

B. Metal Carbonyl Sources

Although the catalyst was severely poisoned during the September, 1993 runs, some improvement in prevention of iron carbonyl deposition on the catalyst was made, as shown in Table 3. Nickel deposition was highly variable, showing no general trend.

Table 3
Iron and Nickel Deposition on the Catalyst
During Methanol Synthesis Runs

Methanol Synthesis Run	Fe Deposited (ppmw)	Fe Deposition /Gas Flow (µg/liter)	Ni Deposited (ppmw)	Ni Deposition /Gas Flow (µg/liter)
September, 1993	946	0.90	471	0.45
April, 1993	3414	0.99	163	0.05
December, 1992	1508	1.58	392	0.41

One possible source of iron and/or nickel carbonyl during the September, 1993 runs was from the steel wool in the gas/liquid separator above the reactor. Steel wool is used for demisting the reactor exit gas of mineral oil. This steel wool was magnetic, indicating that it was not stainless steel, despite contrary labeling. Carbonyls could have formed in the separator, which typically operated at 100°C, and returned to the reactor with the mineral oil. High temperature glass wool will be used in subsequent runs.

The inlet gas is another source of metal carbonyls, even though carbonyl traps should reduce their concentrations. "Hot" traps, which consist of 1" diameter 316 stainless steel tubing filled with alumina pellets and heated to about 300°C, have been used to date. The effectiveness of these traps depends on thermodynamic equilibrium at 300°C favoring the existence of free CO and metal, rather than the metal carbonyl, such that metal carbonyl will decompose in the trap as shown in Equations 1 and 2. Note the large values of the equilibrium constants for the decomposition reactions (Ross, *et al.*, 1964), especially the value for the iron carbonyl decomposition.

This type of trap has been used successfully by previous researchers, but typically with gases that contain relatively low levels of CO (> 10 mole %) at close to atmospheric pressure. Since methanol synthesis requires high partial pressures of CO, the resulting equilibrium metal carbonyl concentration is

relatively high, despite the large equilibrium constants. For the September, 1993 experiment, Table 4 shows estimates of metal deposition on the catalyst from carbonyls which "pass" through the "hot" traps, assuming equilibrium is reached inside the trap. Appendix B contains the detailed metal deposition calculations for each set of process conditions.

Table 4

Iron and Nickel Deposition Calculations
Based on Carbonyls Passing through Traps
for September, 1993 Runs

Run #	Carbonyl Trap Gas In let Temp (°C)	K_{eq} for $Fe(CO)_5$ Decomp. (atm ⁴)	K_{eq} for $Ni(CO)_4$ Decomp. (atm ³)	Total Fe Deposited on Catalyst (ppmw)*	Total Ni Deposited on Catalyst (ppmw)*
1	274	5.7×10^{13}	1.1×10^6	5.9	150000
2	294	2.1×10^{14}	3.6×10^6	2.6	89700
3	294	2.1×10^{14}	3.6×10^6	133	9230000

* Calculated from equilibrium relationship.

Note the extremely high predicted deposition values for nickel. The "hot" traps are essentially useless for methanol synthesis catalyst protection from nickel carbonyls. These traps are much better for iron carbonyl decomposition, but they still "leak" enough iron carbonyl to effectively poison the catalyst. Obviously, the "hot" traps used during the September, 1993 experiment could easily have passed enough metal carbonyls to account for most of the analyzed metal on the catalyst. This does assume, however, that sufficient concentrations of metal carbonyls were initially present in the synthesis gas, since metal carbonyl concentrations were not measured. For future runs, adsorption traps, like activated carbon as demonstrated by Golden, *et. al.* (1991), will be used for metal carbonyl capture.

C. Methanol Synthesis Catalyst Poisoning Mechanisms

Three catalyst samples were analyzed using the X-ray photoelectron spectroscopy (XPS) facility located at University of North Carolina - Chapel Hill. The catalyst samples included: 1) spent catalyst from the April, 1993 methanol synthesis run; 2) spent catalyst from the September, 1993 methanol synthesis run, and; 3) reduced only (i.e., no exposure to carbon monoxide) catalyst. All samples started as BASF S3-86 Cu/ZnO methanol synthesis catalysts. The primary purpose for the analysis was to determine whether the high carbon levels seen earlier on the April, 1993 spent catalyst (August, 1993 Monthly Report) could be attributed to CO disproportionation at metal poisoned sites or to poor washing procedures which left residual mineral oil on the catalyst. The XPS results are shown in Table 5.

Table 5
XPS Results for BASF S3-86 Cu/ZnO Catalyst Samples
(Values in Atomic Percent)

	4/93 Spent	9/93 Spent			Reduced Only		
Total Sputter Time:	0 min Surface	0 min Surface	2 min	14 min	0 min Surface	2 min	12 min
Cu	6.58	16.92	22.65	26.21	15.49	20.87	25.76
Zn	7.07	20.01	23.05	20.98	16.01	18.1	17.36
C	44.51	6.65	2.83	2.90	8.79	4.16	2.15
O	41.84	56.42	51.47	49.91	59.71	56.87	54.73

The most obvious result is that the September, 1993 spent catalyst sample contains far less carbon than the April, 1993 sample. The "reduced only" catalyst contained about the same amounts of carbon as the September, 1993 catalyst. As reported earlier, both of the spent catalysts were poisoned with iron and nickel, but apparently carbon did not form on the September, 1993 catalyst. This difference appears to discredit the hypothesis that iron and nickel catalyze the disproportionation of CO, thereby blocking pores with carbon. This also

suggests that the carbon seen on the April, 1993 catalyst is not "real", i.e. the carbon is probably residual mineral oil.

However, several differences between the April, 1993 and September, 1993 methanol synthesis runs should be considered when making a comparison of the catalyst compositions:

- During the April, 1993 run, the reactor lost all mineral oil, so in essence the reactor was behaving more like a fluidized bed at the end of the run. The September, 1993 run did have 56 mL of oil remaining in the reactor, hence retaining its slurry characteristics.
- The April, 1993 catalyst ran for 14 days, while the September, 1993 catalyst only ran for 7 days.
- The April, 1993 catalyst experienced the 16,500 gas hourly space velocity, 2500 psig run conditions, while the September, 1993 catalyst did not.

These differences could account for some of the difference in carbon between the catalysts. The April, 1993 catalyst will be re-washed with cyclohexane and re-analyzed to ensure that this carbon is not residual mineral oil.

D. High Temperature Mineral Oil Evaluations

Appendix A contains a report on the foaming characteristics and thermal stability of three different mineral oils; Drakeol 10, Drakeol 34, and Ethylflo 180. The evaluation was conducted to help explain oil loss from the stirred autoclave during both methanol synthesis runs and high temperature oil tests. The major conclusions from this report were:

1. Visual observations during refluxing of three high temperature mineral oils and the infra-red spectra of samples of the three boiled oils indicated that there was some thermal degradation of the oils as a result of cracking. Some unsaturation was also observed.
2. A drop in the boiling point of all the three mineral oils was observed when the mineral oil was refluxed for a long period of time.
3. A color change from colorless to yellow occurred for all the mineral oils. This color change suggested some degree of thermal degradation.

4. A foam head about an inch thick formed at the gas/liquid interface when the mineral oils were sparged with nitrogen at ambient temperature. This foam quickly collapsed when the temperature was increased.

Since foaming was observed at ambient conditions, pressurizing or depressurizing the reactor could potentially lead to some oil loss via foaming. Depressurization is also aggravated by dissolved gas coming out of the mineral oil. Therefore, to minimize mineral oil loss, the following precautions will be taken:

- the reactor will be pressurized from two directions, i.e., with the reactor bypass open, so that the mineral oil will experience approximately equivalent pressure at the gas inlet and outlet;
- the reactor will be depressurized slowly over two hours, and;
- upon run completion, the reactor will remain heated while depressurizing to minimize the quantity of dissolved gas in the oil.

These steps should help alleviate mineral oil loss, but they probably will not solve the problem completely.

E. Mineral Oil Recovery/Recycle System Test

A new design of the overhead system on the stirred autoclave reactor was tested. The new system, shown in Figure 5, was designed to minimize pressure drop in the gas line between the reactor and the gas/liquid separator. This minimizes the static liquid head required to return vaporized and condensed oil to the reactor. Also, a water cooling loop was installed inside the separator, similar to a laboratory glassware condenser, to ensure that all mineral oil vapor has condensed. In addition, a liquid level indicator was installed on the gas/liquid separator to monitor liquid buildup in this vessel.

These design changes are intended to improve overall mineral oil retention in the reactor since mineral oil loss has been a significant problem in previous runs. The redesign of the overhead system was based on the theory, supported by calculations, that the pressure drop in the gas exit line exceeds the liquid head that can develop in the gas/liquid separator. Under this condition, condensed liquid cannot return to the autoclave and is blown out of the separator through the gas exit.

Figure 5
Mineral Oil Recovery System - Old and New Design

Old Configuration

New Configuration

A test of the new configuration was conducted, essentially a "blank" run with 175 mL of Drakeol 10 in the reactor and no catalyst present. The reactor conditions during the run were 750 psig pressure, 250°C temperature, and a hydrogen flowrate of 3 slpm. Only hydrogen was used in order to reduce cost and simplify operation. The test lasted for almost 11 days. After completion, the reactor contained 130 mL of mineral oil, i.e., 45 mL of oil was lost. The oil was clear, exhibiting no signs of degradation. The test results were probably skewed by several major pressure surges, i.e., rapid increases in reactor pressure caused by inconsistent gas supply flow and pressure during the run. The liquid level indicator had to be read manually during this test, but all of the readings indicated no buildup of mineral oil in the gas/liquid separator.

As shown in Table 6, the rate of oil loss decreased substantially from previous runs, but still remains too high for reliable, consistent operation.

Table 6
Oil Loss During Stirred Autoclave Runs

Run	Total Oil Lost ¹ (mL)	Oil Lost/Total Gas Flow (mL/liters gas * 1000)
December, 1993 Recovery System Test	45	0.99
October, 1993 Catalyst Reduction	28	2.86
September, 1993 MeOH Synthesis	128	2.81
April, 1993 MeOH Synthesis	175	1.36 ²
December, 1992 MeOH Synthesis	152	3.89

¹All runs had initial oil charges of 175 mL except for the December, 1992 MeOH synthesis which had 225 mL initial oil charge.

²In the April, 1993 MeOH Synthesis run, all of the reactor oil was lost. The 1.36 oil loss rate is conservative since the exact time when all of the oil was lost is not certain.

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APPENDIX A

MINERAL OIL EVALUATIONS

**NORTH CAROLINA STATE UNIVERSITY
DEPARTMENT OF CHEMICAL ENGINEERING**

**HIGH TEMPERATURE STUDIES AND I-R
ANALYSIS OF MINERAL OILS USED FOR
HIGHER ALCOHOL SYNTHESIS IN A
SLURRY REACTOR**

DATE : 10th January 1994.

By: Deval (Dave) P. Parikh

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SUMMARY

The overall objective of the high temperature studies and subsequent I-R analysis of the "heated" mineral oils was to see if there was any presence of unsaturation in the mineral oil after exposing it to high temperature in an inert nitrogen environment. The flowrate of nitrogen was set to be the same as the flowrate of synthesis gas in the stirred autoclave reactor. It was also desired to observe the foaming characteristics of the mineral oils.

Foaming was present at low temperatures, but an insignificant amount of foam was present at high temperatures. A substantial drop in the boiling point temperature, and a change in color of the mineral oil was observed when the system was allowed to reflux for a long period of time.

An extensive I-R analysis revealed the presence of unsaturation in the "heated" mineral oils. This unsaturation can be attributed to the phenomenon of thermal cracking and thermal degradation. In order to quantify the amount of unsaturation, a wet chemistry method is also outlined.

It is recommended that similar runs using a magnetic stirrer and a synthesis gas inlet feed stream be done in the future.

INTRODUCTION

Mineral oils are extensively used in cosmetics, pharmaceuticals, the food industry as well as the plastic industry. In the slurry reactor system used for the manufacture of higher alcohols, mineral oil is used as a slurry medium in which the catalyst is suspended, and through which the synthesis gas is bubbled.

For the higher alcohol synthesis runs which are to be done at a temperature between 350°C and 420°C, and a pressure range of 1000psig to 1500psig it is necessary to find a suitable slurry medium. At these reactor conditions it is important to make sure that the mineral oil used for this process is chemically stable and chemically inert (6). It is also vital to see whether the foaming characteristics of the mineral oil at the reactor conditions can account for the possible loss of mineral oil that occurred during the 5/93 and 9/93 runs.

Various mineral oils were considered for the high temperature studies. These included Drakeol-10 & Drakeol-34 (made by Penreco) and Ethylflo-180 (made by Ethyl Corporation). Appendix A shows the different characteristics of the mineral oils which include boiling point, chemical composition, vapor pressure, specific gravity and average molecular weight.

EQUIPMENT AND PROCEDURE

High Temperature Mineral Oil Studies :

The apparatus used for the high temperature mineral oil studies included a distilling flask, electric heating pad, thermometer, condenser, a gas dispersion tube and a burette which was used as a soap bubble flowmeter.

The amount of mineral oil used in the stirred autoclave reactor was 175ml. The same amount of mineral oil was poured in a three-necked distilling flask, and a heating pad was then placed around the flask. The condenser was fitted on the central neck and was made air tight by applying high temperature grease-"Grease H". The thermometer was attached to the left neck and the gas dispersion tube was fitted to the right neck. Care was taken that all the three necks of the distilling flask were greased properly. The top of the condenser was connected to a 100ml burette which functioned as a soap bubble flowmeter. This burette was used monitor the nitrogen flowrate as it was used to measure the flow rate of the exit gas from the condenser. The flowrate of nitrogen through the mineral oil was calculated to be 59.1 ml/min (Appendix B), which is close to the synthesis gas flow rate through the reactor. The whole apparatus is setup in a hood.

The condenser water was turned on first, and the nitrogen flow at the desired flowrate was then started. The heating was turned on next. At five minute intervals (or as required), the temperature and the corresponding observation was recorded (Appendix C). Three different runs for the three different mineral oils, Drakeol-10, Drakeol-34 and Ethylflo-180, were carried out. To avoid any heat loss to the surroundings the flask, was covered with aluminum foil. In order to check for possible thermal degradation and thermal cracking an Infra- Red(I-R) analysis of the sample was carried out.

I-R Analysis :

The RFX-65 Fourier Transform Infra--Red (FTIR) spectrometer manufactured by Laser Precision Analytical was used for the I-R analysis of the mineral oils. A Calcium Fluorite cell was used for sample analysis.

It was determined that the mineral oil had to be diluted using a solvent in order to get the peaks of the I-R spectrum within scale. The mineral oil was mixed in a 1:9 ratio with cyclohexane (solvent) in a 10ml measuring cylinder. The lower Teflon screw of the cell was initially kept closed. The cell was then placed upright, and the mineral oil solution was added drop-wise using a dropper. After the cell was almost filled, the Teflon screw was carefully fitted on the top so that there were no bubbles present in the cell. The cell was then dried to avoid any evaporation of the solvent in the ionization chamber. In order to get a good spectrum it is important to avoid the presence of any bubbles in the cell.

The cell was then set in the ionization chamber of the FTIR apparatus, 64 scans of the sample were taken, and the mean of these scans was then saved using the software accompanying the FTIR. A detailed procedure on how to use the FTIR and the complementary software is given in Appendix D. The cell was then cleaned by flushing it with cyclohexane. Since the focus of these studies was to see the possible change in composition of the mineral oil, it seemed logical to have the spectra of the pure mineral oil as the background spectrum and that of the "heated" mineral oil as the main spectrum. Thereby, the difference spectra which is of prime interest can be obtained. Hence the spectrum of Drakeol-10(pure) was taken and saved as background. This was followed by taking the spectrum of Drakeol-10(heated). The same process was repeated for Drakeol-34 and Ethylflo-180.

RESULTS AND DISCUSSION

High Temperature Oil Studies :

For the three oils that were studied the following basic trend was observed :

- > As nitrogen flow was started, foam, about 1 inch high was initially present
- > When low-moderate heating was applied to the mineral oil, the foam almost disappeared.
- > A thermal gradient was observed when temperature was raised above 250°C. This can be explained by the fact that different densities exist within the mineral oil because it has hydrocarbons with substantially different molecular weights. It also suggested that the oil was not very well mixed.
- > The mineral oil reaches its boiling point (at 1 atm) and the temperature remains constant for a period of 15-20 minutes. Then there is a significant drop in temperature (20°C-40°C) which can be explained by the phenomenon of thermal cracking of straight chain hydrocarbons. As the hydrocarbon chain splits, hydrocarbons with lower molecular weights are formed which results in the lower boiling point of the mineral oil.
- > When the system was allowed to run for a period of about 20 hours a major discoloration of the mineral oil i.e. from colorless to yellow occurred. This can also be explained by the phenomenon of thermal cracking. A detailed analysis of this phenomenon is explained in Appendix E. The color change, the observed boiling point temperatures and the final temperatures for the three mineral oils studied is summarized in Table 1.

TABLE 1

Oil	Color Change	Observed Boiling Point Temperature	Observed Final Temperature
Drakeol-10	colorless-->sunset yellow	385°C	354°C
Drakeol-34	colorless-->golden yellow	358°C	326°C
Ethylflo-180	colorless-->light yellow	378°C	322°C

Apart from the general tendencies of the mineral oil, the following exceptions should be noted :

- > 1.2ml of Drakeol-34 was present in the burette which passed through the condenser without being condensed.
- > When nitrogen started flowing through Ethylflo-180 the foaming was so so intense that the oil entered the condenser.
- > From the table it is evident that there was a major drop in boiling point temperature (56°C) for Ethylflo-180.

I-R Analysis :

The mineral oils studied were primarily made up of a saturated straight chain as well as branched chain hydrocarbons. Since the exact composition of the mineral oils cannot be known, it was difficult to decipher the changes in composition. However, to get an approximate idea about the possible composition change an I-R analysis was carried out. The transmittance I-R spectra of the three mineral oils Drakeol-10 (Figure 1), Drakeol-34 (Figure 2) and Ethylflo-180 (Figure 3) are attached.

The analysis of Drakeol-10 is as follows :

- > The strong peak at 1450cm^{-1} indicated the presence of $-\text{CH}=\text{CH}_2$ groups and/or $>\text{C}=\text{CH}_2$ groups(5). In order to explain the unsaturation of hydrocarbons, and the probable presence of olefins, a possible theory is explained in detail in Appendix E.
- > When a long chain hydrocarbon chain is cracked to smaller chains the resulting molecules have a different configuration and possible unsaturation. Hence the saturated carbon atom adjacent to the unsaturated carbon atom will vibrate at a different frequency than previously observed for the pure mineral oil. The strong peaks between 2850cm^{-1} and 2975cm^{-1} , and the peak at 2650cm^{-1} in the difference spectrum suggested the presence of $\text{C}-\text{CH}_3$ groups as well as the presence of $-\text{C}-\text{CH}_2$ groups (6,9) which can be attributed to the phenomenon of thermal cracking (Appendix E).
- > The weak peak at 1375cm^{-1} (9) indicates the possible presence of a tertiary butyl group $(\text{CH}_3)_3\text{C}-$ group.

Similar I-R spectra are observed for both Drakeol-34 and Ethylflo-180. In addition to the peaks explained above, Ethylflo-180 has an additional peak. The extra peak

FIGURE 1

FN:TRDR-103 FILE:IR SPECTRA OF DRAKEDL-10 AFTER HIGH TEMP STUDIES
 DS1:TRANSMITTANCE SPECTRA
 DS2:

X=VN Y=trns DATE=Mon Oct 25 16:13:23 1993 MODEL=RFX-65
 SCNS=64/128 GAIN=4.00/4.00 RESD=2.000 APDD=NB-M DET=IGSI0

FIGURE 2

FN: TRDR-343 TITLE: IR SPECTRA
 DSI: TRANSMITTANCE SPECTRA
 DSI: 2
 X=VN Y=trns
 SCNS=64/128
 DATE=MON OCT 25 16:59:47 1993
 GAIN=4.00/4.00 RESN=2.000
 MODEL=RFX-65
 APD=NB-H DET=TGSI0

FIGURE 3

FN: TRETFLD-3 TITLE: IR SPECTRA OF ETHYLENE AFTER HIGH IMP S.O.D.S
 DS1: TRANSMITTANCE SPECTRA
 DS2:
 X=WN Y=trns
 SCNS=64/128
 DATE=MON OCT 25 17:47:01 1993
 GAIN=4.00/4.00 RESO=2.000
 MODEL=RFX-65
 APD=NB-M DET=IGSI0

at 1450cm^{-1} is probably due to the CH_2 scissor vibration or a CH_3 anti-symmetric deformation (5).

Thus, the I-R analysis of the difference spectra gives a qualitative measure of the type of compounds present in the mineral oils. In order to get a quantitative measure of the degree of unsaturation a possible wet chemistry technique is suggested in Appendix F.

CONCLUSIONS

1. From the observations during the high temperature mineral oil studies and the results of the I-R spectra of the 3 samples of mineral oil, it was clear that there was some thermal degradation of the oils as a result of cracking. A certain degree of possible unsaturation was also observed. However, it should be noted that the runs were carried out in a nitrogen environment while the reactor runs are done with an inlet feed stream of CO, CO₂ and H₂ which can lead to different results.
2. A drop in the boiling point of all the three mineral oils was observed when the mineral oil was heated for a long period of time.
3. There was a color change from colorless to yellow for all the mineral oils which was added evidence to the phenomenon of thermal cracking.

RECOMMENDATIONS AND POSSIBLE FUTURE WORK

1. It is recommended that a magnetic stirrer be used for agitation when the mineral oil is heated to get uniform mixing and to minimize the presence of thermal gradients.
2. An inlet feed stream of synthesis gas, similar to the reactor inlet feed should be used to analyze what actually happens to the mineral oil under reactor conditions.
3. Similar runs should be done in a high pressure system which goes up to 1500psig to simulate reactor conditions closely.
4. The wet chemistry method outlined in Appendix F should be used to determine the degree of unsaturation in the mineral oils.

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APPENDICES TO APPENDIX A

APPENDIX A-1:

TABLE OF PROPERTIES OF MINERAL OILS

TABLE 2
HIGH TEMPERATURE OILS (6)

NAME	MANUFACTURER	COMPOSITION	BOILING Pt. DISTILLATION	VAPOR PRESSURE	SPECIFIC GRAVITY	AVERAGE MOL. WT.	COMMENTS
DRAKEOL-10	Penreco	Mineral Oil- 65% Paraffinic 35% Napthenic	283 C IBP 407 C 50% 481 C 90%	< 1mm Hg	0.838-0.864	366	Currently used for <300 C operation
DRAKEOL-34	Penreco	Mineral Oil- 68% Paraffinic 32% Napthenic	437 C IBP 489 C 50% 529 C 90%	< 1mm Hg	0.858-0.872	492	Mixture or longer hydrocarbon chains compared to DRAKEOL-10
ETHYLFLO-180	Ethyl	Hydrogenated homopolymer of 1-decene	Not available	< 1mm Hg	0.845-0.855	2000	Mixture of C40, C50, C60 and C70 paraffins, contains some branched products

APPENDIX A-2:

FLOWRATE CALCULATIONS

Calculation for the flow-rate required for the experimental set-up simulating reactor conditions.

→ The reactor operates at $T = 250^\circ\text{C}$ } MeOH
 $P = 750 \text{ psig}$ } synthesis.

Assuming that the ideal gas law holds

$$\left. \begin{array}{l} T_1 = 250^\circ\text{C} = 523\text{K} \\ P_1 = 750 \text{ psig} \\ V_1 = ?? \end{array} \right\} \text{Reactor condition}$$

$$\left. \begin{array}{l} T_2 = 25^\circ\text{C} = 298\text{K} \\ P_2 = 14.7 \text{ psig} \\ V_2 = 3102.5 \text{ sccm} \end{array} \right\} R_n$$

$$\therefore V_1 = \frac{P_2 V_2}{T_2} \times \frac{T_1}{P_1}$$

$$\therefore V_1 = 106.72 \text{ cc/min.}$$

Internal reactor diameter = $D_R = 4.6 \text{ cm}$.

$\therefore$ Area for gas flux on the Liquid-Vapor inter face.

$$\text{Area}_R = 16.62 \text{ cm}^2$$

Volume of experimental ^{distilling} flask = 250 ml.

Volume of mineral oil = 175 ml

Using mathematical tables on pg 1-27 (Perry's

$$\frac{\text{Segmented Volume}}{\text{Spherical Volume}} = 0.3.$$

$$\therefore \text{Corresponding } \frac{h}{D} \text{ ratio} = 0.37$$

$$\Rightarrow \boxed{h_e = 2.89 \text{ cm}}$$

$$\therefore \frac{h}{R} \text{ ratio} = 0.74$$

$$\therefore \text{Corresponding central angle} = \theta = 150$$

$$\therefore \frac{\text{Area}}{R^2} \text{ ratio} = 1.0589$$

$$\therefore \text{Area} = (15.272) \times (1.0589)$$

$$\therefore \boxed{\text{Area}_e = 16.17 \text{ cm}^2} = \text{surface area of experime setup}$$

→ gas flow at the rate of 106.7 cc/min in the reactor.

∴ A corresponding flow-rate in the experimental setup at STP

$$\frac{106.7 \times 16.17}{16.62} = 103.8 \text{ cc/min}$$

Set up.

$$\left\{ \begin{array}{l} P_1 = 14.7 \text{ psi} \\ V_1 = ? \\ T_1 = 298^\circ \text{K} \end{array} \right.$$

$$\left\{ \begin{array}{l} P_2 = 14.7 \text{ psi} \\ V_2 = 103.8 \text{ cm} \\ T_2 = 523. \end{array} \right.$$

$$\therefore V_1 = \frac{V_2}{T_2} \times T_1$$

$$\therefore V_1 = 59.14 \text{ cm}$$

$\therefore$ A volume of 59.14 cm should be used in the experimental setup.

APPENDIX A-3:

LABORATORY DATA

Aim: To check as to whether the mineral oil foams at the boiling point as well as at other temperatures.

Apparatus:

Oil Used: - Drakeol 34 175 ml

175 ml = Reactor volume of oil.

Observation:

Time

3:30 pm.

Temp (°C)

22°

Observation.

The oil started foaming as soon as the N_2 flow was turned on. The foam was about $1\frac{1}{4}$ - $1\frac{1}{2}$ above the liquid level.

TIME	TEMP (°C)	OBSERVATION
3:49 pm	~ 175 °C	foam decreased to about 1/3" above mineral oil level
3:52 pm	182 °C	foam was about 1/2" above the mineral oil level. → signs of condensate in
3:59 pm	190 °C	
4:05 pm	225 °C	foam reduced to about 1/4" above mineral oil
4:10 pm	255 °C	foam height is almost negligible
4:15 pm	275 °C	"
4:20 pm	293 °C	absolutely no presence of foam. Bubbling because of N ₂ flow to the fitted disc.
4:25 pm	305 °C	"
4:30 pm	313 °C	"
4:35 pm	→	pro shut down run.

Aim To verify ~~on~~ the foaming characteristics of Draked 34 at reactor-like conditions, using the calculated required flow-rate.

Observations:

<u>TIME</u>	<u>TEMP</u>	<u>OBSERVATIONS</u>
4:35 pm	22°C	foam observed about $\frac{1}{2}$ " above oil level.
4:40 pm	~60°C	foam reduced to about $\frac{1}{4}$ " above oil level.
4:45 pm	131°C	"
4:50 pm	177°C	foaming about $\frac{1}{4}$ " but more concentrated on the sides.
4:55 pm	224°C	negligible foaming, but still presence of a rim of bubbles on the sides.
5:00 pm	252°C	"

From now on, ~~use~~ the temperature should be maintained at reaction temperature i.e. 280°C.

5:05 245°C turned valve to 55%, which caused the, 25

5:10

244°C

turned up variac
to 80%.

→ An increase in outlet gas flow-rate increased

5:15

254°C

variac around 75%.

5:30

252°C

shut down.

Aim: To verify the foaming characteristics of Dracol-34 at its boiling point and to see the extent of discoloration of the ~~red~~ mineral oil.

Observations:

→ set N_2 flow-rate to $\sim 60 \text{ cc/min}$.

Time

Temperature

3:03 pm

22°C

3:18 pm

183°C

3:33 pm

277°C

3:48 pm

323°C

Observations

Started heating mineral oil

→ as soon as the heating was turned on, the foam almost disappeared

→ Initially when the flow-rate was being adjusted there was a presence of foam

Note: This is the same mineral oil that was used in the previous runs done on 10/01 & 10/04

presence of $\frac{1}{4}$ " of foam

negligible foam

thermal gradient was observed - primarily because of the presence of different densities with the mineral oil.

Indication: Oil is not as w

4:03 pm

339°C

Same as before
→ droplets of condensate seen at the lower end of the condenser

4:18 pm

342°C

"
+ signs of condensate all over the condenser

4:28 pm

342°C

"

4:33 pm

342°C

→ seems like the boiling point of the mineral oil has been reached - sooner than expected!!
Expected boiling point is 398°C (from previous run)

→ Explanation: the same oil was heated for a couple of previous runs

→ oil refluxing in all sides of the flask.

→ distinct white fumes observed on the top of the flask - (bottom of condenser)

4:43 pm

342°C

→ " "
→ no signs of discoloration yet.

4:53 pm

342°C

→ refluxing is fairly vigorous.

5:03 pm

341°C

→ Drop in boiling temp.

5:08 pm

→ wrapped flask with aluminium foil

5:13 pm

345°C

An increase in temp
because of better insula

5:18 pm

357°C

"

5:23 pm

370°C

"

+ → much more fumes
observed - perhaps because
of better insulation

5:28 pm

378°C

very vigorous reflux
through condenser
→ almost twice as fast.

5:33 pm

384°C

"

5:38 pm

385°C

→ Temp. almost constant

10/09

12:22 pm

354°C

→ Oil refluxing very
vigorously

→ Drop in temperature (bp)
perhaps because of the
breaking up of long chain
hydrocarbons.

→ presence of a narrow rim of
bubbles on the sides.

→ major discoloration of the
mineral oil has occurred.
Color has changed from
colorless → sunset yellow.
(yellow-orange).

→ Shut down the heating.

→ presence of about 1.2 ml of
yellow liquid in burette,
that is used as a flow-meter.
Perhaps due to the presence
of mineral oil that

<u>Time</u>	<u>Temp.</u>	<u>Observations</u>
12:32pm	265°C.	did not condense, over the condenser. This still forms bubbles in the burette (like snoop!).
12:42pm	207°C	Thickness of foam increased to about $\frac{1}{3}$ "
		→ shut N_2 flow-rate
		→ immediate disappearance of foam
12:47pm	189°C	→ shut down condenser water.

Recommendations:

- Analysis of mineral oil
- Analysis of burette sample.

Aim: To verify the foaming characteristic of Dreckel-10 at its boiling point and to see the extent of discoloration of the mineral oil.

Observations:

→ set N_2 flow-rate to ~ 60 cc/min

Time

Temp

Observation

4:00 pm

25°C

→ foam about $\frac{2}{5}$ Pre

4:10 pm

109°C

→ foam just present ~~above~~ on the rim of the flask about $\frac{1}{4}$

4:20

225°C

→ absolutely no foam observed.

4:25

265°C

→ thermal gradient at primarily because of presence of different oil within the mineral oil might not be uniform.
→ Signs of reflux on the S of the flask.

4:30

295°C

4:35

320°C

4:40

340°C

→ Refluxing vigorously

Time.	Temp.	Observation
4:45pm	355°C	→ refluxing fairly vigorously. → seems that boiling point is almost reached

4:50pm	358°C	→ refluxing very vigorously even from the condenser. → no presence of visible fumes (white/colorless)
--------	-------	---

4:55pm	359°C	→ "
--------	-------	-----

5:10pm	357°C	→ Drop in boiling temp. → Perhaps, due to splitting of long-chain hydrocarbons
--------	-------	---

5:40pm	355°C	→ "
--------	-------	-----

5:55pm	354°C	→ condensing Mineral oil refluxing extremely vigorously.
--------	-------	--

1/14 12:10pm	326°C	→ oil refluxing very vigorously.
--------------	-------	----------------------------------

		→ Drop in boiling temperature perhaps due to formation of unsaturated hydrocarbons
--	--	--

		→ color change from colorless → golden yellow.
--	--	--

12:15pm	325°C	→ shut off heating
---------	-------	--------------------

U/a.b/4/15. Hydro temperature - on foaming curves

Aim: To study the foaming characteristics of Ethyl-Flo at its boiling point and to see the extent of discoloration of the mineral oil.

Observations:

→ set N_2 flow rate to ~ 60 cc/min.

Time

Temp.

Observations

8:45 pm

24°C

→ immense foaming.
The whole flask was full of bubbles. Oil was present even on the 5m coil of the condenser, by the time the flow-rate was adjusted. This is because of the high viscosity of the mineral oil.

8:55 pm

92°C

→ foaming reduced considerably to about $\frac{1}{3}$ "

9:00 pm

199°C

→ foaming reduced to about $\frac{1}{4}$ "

→ oil, that was in the condenser coil, started dripping back into the flask.

9:05 pm

260°C

→ foaming actually increased to about 0.7" - This is not quite a typical trend for

9:10 pm

295°C

→ still about 0.7" of foam is present. The bubbles are very small & quite closely packed together.

9:15 pm

325°C

"

9:21 pm

356°C

→ foam about the height of 0.5" is present above the mineral oil level.

→ presence of white fumes just before the gas enters the condenser.

→ first signs of reflux

→ thermal gradient observed substantially, primarily because of the high viscosity of the liquid.

9:27 pm

378°C

→ foam height reduces to about 1/3"

→ mineral oil is refluxing very vigorously.

→ the oil present in the condenser coils, acts as a blockage to the mineral oil vapors. Thus, the flow rate of the gas is through the burette is highly

(disorganized) random (disrupt) presence of brown debris in the mineral oil - probe from the grease.

9:37 pm

357°C

→ drop in temp - Surprising!

9:47 pm

345°C

→ presence of brown spots in the first condense coil.

Time

Temp.

Observation.

9:57pm.

346°C

- mineral oil - refluxing just as before.
- almost no foam present whatsoever.
- as it appears that the boiling point has been reached (considering there has been some decomposition)

7/27. 1:50pm.

322°C

- turned-off the heating.
- mineral oil has changed color from colorless → straw (light yellow).
- oil refluxing extremely vigorously.
- no appearance of foam

APPENDIX A-4:

FTIR INSTRUCTIONS

FTIR User's Operating Instructions

Data Collection

1. Turn on display by pressing the "on" switch on the lower left of the screen.
2. Move to your subdirectory using the >cd command.
(Outside users: Go to the guest subdirectory by typing >cd \FTIR\GUEST.)
3. Set the operating parameters using the >AQPARM command.
(Outside users: Type >AQPARM LOAD TGS to set the default operating parameters for the TGS detector.) MCT TGS o.
4. Check that screen is not in right front slot of chamber; if it is, move to back slot. ←
5. Insert cell or sample to be used as background into beam. Allow to purge approximately 1 minute. NOTE: If using liquid samples, be sure to wipe outside of cell dry so that no vapors are created in sample chamber. Be sure to check around filling ports and plugs of cells.
6. Type >AUTOGAIN. (This can be done during purge.) Note gain value displayed when cursor returns.
7. The gain can be checked by typing >TSTB. The spectrum displayed should not go above 70%. Press <esc> to stop the TSTB function. If the transmission is above 70%, reduce the gain by typing >AQPARM GAIN=n, where n is less than the value noted in #6.
8. When purge is complete, acquire background by typing >AQBK.
9. Load sample. See note in #5. Allow to purge.
10. Acquire spectrum of sample by typing >AQSP name (for transmission spectrum) or >AQSA name (for absorption spectrum). The spectrum name can be 8 characters maximum.
11. Repeat #8 and #10 with other samples.
12. When finished, type >IBM to leave data collection mode.
13. Transfer files to floppy disk (3.5" or 5.25"). Files left in the guest directory will be cleared without notice. sp
13. Turn off screen by pressing the "on" switch if finished with computer.
14. Record date, name, and any comments in FTIR log book.

ANYONE NOT USING LOG BOOK WILL LOSE OPERATING PRIVILEGES.

APPENDIX A-5:

POSSIBLE THEORY FOR THE THERMAL CRACKING PHENOMENON

POSSIBLE THEORY FOR THERMAL CRACKING

The following discussion is a conceivable explanation of the phenomenon of thermal cracking and thermal degradation that is observed in the high temperature studies of the three different mineral oils. Suppose we have a hydrocarbon chain as under (1,2):

Since the bond dissociation energy of even the tertiary C-H bond is in the order of 91-98 Kcal/mol (Table 3), and that of the various C-C bonds is of the order of 78-85 Kcal/mol, it is more likely that the C-C bond in the long chain hydrocarbon is broken. This will result in the generation of two free radicals :

Hence the first radical can undergo the following transformation resulting in an alkene formation (1).

Thus the alkyl (R^{IV}) group which was initially attached to the $-CH_2-\overset{\overset{R^I}{|}}{\underset{\underset{H}{|}}{C}}-CH_2-R^{II}$ group is now adjacent to the $-C=CH_2$ (alkene) group. This might cause the alkyl group to vibrate in a different manner than before which is justified by the presence of $C-CH_3$ and $C-CH_2-$ group peaks in the $2650\text{ cm}^{-1} - 2975\text{ cm}^{-1}$ region.

It should be noted that this is just a probable explanation to the thermal cracking phenomenon. Since this kind of mechanism generates free radicals which in turn react with other free radicals to give alkenes. It is thus an extremely complicated process, especially because we do not know the exact composition and concentrations of the initial mineral oil.

APPENDIX A-6:

WET CHEMISTRY METHOD TO
DETERMINE THE AMOUNT OF
UNSATURATED HYDROCARBONS

WET CHEMISTRY METHOD TO DETERMINE THE AMOUNT OF UNSATURATED HYDROCARBONS

1. Add a measured amount of Bromine-water solution, which is excess to possible alkenes present in the mineral oil sample. The bromine-water solution which is dark brown in color will react with the unsaturated alkene to give a saturated alkyl bromide. The alkyl bromide thus formed is colorless. The basic reaction is as follows (1) :

2. Since the bromine-water solution is in excess, even if all the unsaturated hydrocarbons are reacted to form bromides the color of the mixture will still remain brown. Thus a back titration of the solution with a reducing agent like stannous chloride (SnCl_2) or sodium dithionite solution, at a fixed concentration of the solution should be performed. Record the amount of sodium dithionite added. The reaction of sodium dithionite with Bromine is illustrated as under :

Assuming that the reaction is elementary, the stoichiometry of the reaction yields the amount of excess Bromine present in the mixture. Find the amount of excess Bromine present, subtract this amount from the initial amount added. This will give the amount of Bromine needed for the formation of alkyl bromides from the unsaturated hydrocarbons.

APPENDIX B

METAL CARBONYL DECOMPOSITION

EQUILIBRIUM CALCULATIONS

Carbonyl Equilibrium

Nickel and Iron Carbonyl Formation -					
Dependence of Ka (Equilibrium Constant) on Temperature					
Based on equations developed by Ross, et.al. Journal of Chemical and Engineering Data, Vol 9, No. 3, July 1964, pp 339-340.					
For Ni(CO)4: log Ka = 8546/T - 21.64 (T in Kelvin)					
For Fe(CO)5: log Ka = 8940/T - 30.09 (T in Kelvin)					
TEMP (K)	1000/T	logK (FeCO5)	logK (NiCO4)	K (FeCO5)	K (NiCO4)
273	3.66	2.66	9.66	4.54E+02	4.61E+09
373	2.68	-6.12	1.27	7.55E-07	1.87E+01
473	2.11	-11.19	-3.57	6.47E-12	2.68E-04
573	1.75	-14.49	-6.73	3.25E-15	1.88E-07
673	1.49	-16.81	-8.94	1.56E-17	1.14E-09
773	1.29	-18.52	-10.58	2.99E-19	2.60E-11
873	1.15	-19.85	-11.85	1.41E-20	1.41E-12
973	1.03	-20.90	-12.86	1.25E-21	1.39E-13
Calculation of Carbonyl Concentration Leaving the Carbonyl Trap					
September, 1993 Methanol Synthesis Run # 1					
Temperature:	274.2	C	Tc:	132.9	K
Pressure:	750	psig	Pc:	34.9	atm
y CO :	0.51				
GHSV:	5000	sl/kg cat/hr			
Run Time:	77	hr			
Pr:	1.49				
Tr:	4.12				
log f/P =	0.029	(from Reid, Prausnitz, and Sherwood, "The Properties of			
f CO =	28.37	atm	Gases and Liquids", 3rd Edition,		
			McGraw-Hill, 1977)		
Ka Fe(CO)5 =	1.75E-14				
Ka Ni(CO)4 =	9.41E-07				
Gas Mole Frac Fe(CO)5 =	6.18374E-09	Assuming elemental Fe and Ni are present			
Gas Mole Frac Ni(CO)4 =	0.011710078	on the trap adsorbent (alumina pellets)			
Total Fe(CO)5 Conc =	5.935593151	ppm on the catalyst surface			
Total Ni(CO)4 Conc =	153459.5297	ppm on the catalyst surface			
Calculation of Carbonyl Concentration Leaving the Carbonyl Trap					

Carbonyl Equilibrium

September, 1993 Methanol Synthesis Run # 2					
Temperature:	293.6	C	Tc:	132.9	K
Pressure:	750	psig	Pc:	34.9	atm
y CO :	0.51				
GHSV:	10000	sl/kg cat/hr			
Run Time:	60	hr			
Pr:	1.49				
Tr:	4.26				
log f/P =	0.029	(from RPS)			
f CO =	28.37	atm			
Ka Fe(CO)5 =	4.83E-15				
Ka Ni(CO)4 =	2.75E-07				
Gas Mole Frac Fe(CO)5 =	1.70671E-09				
Gas Mole Frac Ni(CO)4 =	0.003420651				
Total Fe(CO)5 Conc =	2.5530747	ppm on the catalyst surface			
Total Ni(CO)4 Conc =	89654.6395	ppm on the catalyst surface			
Calculation of Carbonyl Concentration Leaving the Carbonyl Trap					
September, 1993 Methanol Synthesis Run # 3					
Temperature:	293.6	C	Tc:	132.9	K
Pressure:	2500	psig	Pc:	34.9	atm
y CO :	0.51				
GHSV:	16500	sl/kg cat/hr			
Run Time:	8	hr			
Pr:	4.90				
Tr:	4.26				
log f/P =	0.09	(from RPS)			
f CO =	107.36	atm			
Ka Fe(CO)5 =	4.83E-15				
Ka Ni(CO)4 =	2.75E-07				
Gas Mole Frac Fe(CO)5 =	4.02853E-07				
Gas Mole Frac Ni(CO)4 =	0.213352985				
Total Fe(CO)5 Conc =	132.5784364	ppm on the catalyst surface			
Total Ni(CO)4 Conc =	9226707.017	ppm on the catalyst surface			
TOTAL Fe :	141.0671043	ppm on the catalyst surface			
TOTAL Ni:	9469821.186	ppm on the catalyst surface			

APPENDIX C

**CALCULATION OF REDUCED RATE
CONSTANT BASED ON ROBERTS, et al.,
LINEAR DEACTIVATION MODEL**

Determination of $k'(t)/k^*(t)$ Based on Linear Deactivation Model

Step 1 - Determine Concentrations of Iron and Nickel on Catalyst Surface

Iron and Nickel Bulk Concentrations (from Inductive Coupled Plasma Analysis)

	Concentrations (ppm)		
	Fresh Catalyst	Spent Catalyst	Deposited
Iron	34	980	946
Nickel	56	527	471

Catalyst Weight in Reactor = 37.23 g

BET Surface Area = 91 m²/g (from Air Products data for reduced BASF S3-86 Cu/ZnO catalyst)

* Assume the deposited metal is all on the surface

Concentration of metal on surface

$$C_{Fe} \text{ (g Fe/m}^2\text{)} = (946 \text{ g Fe}/10^6 \text{ g catalyst}) / (91 \text{ m}^2/\text{g catalyst}) = 1.04 \times 10^{-5} \text{ g/m}^2$$

$$C_{Ni} \text{ (g Ni/m}^2\text{)} = (471 \text{ g Ni}/10^6 \text{ g catalyst}) / (91 \text{ m}^2/\text{g catalyst}) = 5.18 \times 10^{-6} \text{ g/m}^2$$

Step 2 - Linear Model

$$k'(t)/k^*(t) = 1 - \alpha_{Fe}C_{Fe} - \alpha_{Ni}C_{Ni}$$

* Use α 's determined by Roberts, et al. (1993)

$$\alpha_{Fe} = 54 \times 10^3 \text{ m}^2/\text{g Fe}$$

$$\alpha_{Ni} = 98 \times 10^3 \text{ m}^2/\text{g Ni}$$

$$k'(t)/k^*(t) = 1 - (54 \times 10^3)(1.04 \times 10^{-5}) - (98 \times 10^3)(5.18 \times 10^{-6}) = -0.06859$$

**DATE
FILMED**

10/17/94

END