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Patent Caution

Novel Approaches To The Production of Higher Alcohols From Synthesis Gas

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NOVEL APPROACHES TO THE PRODUCTION OF HIGHER ALCOHOLS FROM SYNTHESIS GAS

Quarterly Technical Progress Report
January 1, 1997 though March 31, 1997

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 (complete).

Task 4. Synthesis of Higher Alcohols via Acid-Base Catalysis (complete).

Task 5. Technology Evaluation (complete).

SUMMARY

A modified analytical system was assembled and calibrated, in preparation for a second run with cesium (Cs)-promoted "zinc chromite" catalyst. A new column for the on-line gas chromatograph (GC) was purchased for the analysis of various light olefin and paraffin isomers.

A run was carried out in the continuous stirred autoclave using the Cs-promoted catalyst. Decahydronaphthalene was used as the slurry liquid. Reaction conditions were: 375°C, 2000 psig total pressure, 0.5 H_2/CO ratio, and; 5000 sL/Kg (cat.)-hr. Analysis of the data from this run is in progress.

A manuscript on the thermal stability of potential slurry liquids was submitted to *Industrial and Engineering Chemistry Research.*

A paper entitled "The Effect of Liquid Composition on the Performance of "Zinc Chromite" Catalyst in a Slurry Reactor" was presented at the 1997 Spring National Meeting of the American Institute of Chemical Engineers in Houston, Texas.

TECHNICAL DETAILS

A. Analytical Systems

Based on the studies that were conducted during the preceding quarter, a new analytical system was designed. This system will be used for a run with cesium (Cs)-promoted "zinc chromite" catalyst.

The new analytical system will be configured as follows. First, the effluent from the stirred autoclave reactor, after leaving the back-pressure regulator at a pressure of about 50 psig, will pass through a dry ice/acetone condenser which will operate at approximately -78°C. This will condense most of the methanol, essentially all of the higher alcohols, essentially all of the vaporized slurry liquid (decahydronaphthalene), and varying amounts of olefins and paraffins, depending on carbon number. This condensate will be collected on a daily basis. The analysis of each liquid sample will be used in all material balances for the day over which the liquid sample was collected. The liquid analysis will be done off-line, either in the Chemistry Department's GC/MS (mass spectrometry) facility or with the 25 m Poroplot Q capillary column that is part of the existing GC system, operating isothermally at 150°C.

The gas leaving the condenser will pass into the on-line, dual-column GC. As usual, the fixed gases (H_2, N_2, CO, CO_2, and H_2O) will be analyzed using a 1.5m Carboxen 1000 packed column connected to a thermal conductivity detector (TCD). The hydrocarbons will be analyzed with a newly-purchased column, a 30m GasPro GSC capillary column, connected to a flame ionization detector. Argon will be the carrier gas. Both columns will be operated isothermally at 150°C. The GasPro column is not capable of

analyzing alcohols. However, any uncondensed alcohols that are fed to this column will not interfere with the analysis of olefins and paraffins.

A 25 m Poroplot Q capillary column will be used for analysis of lower alcohols and dimethyl ether (DME), and to provide a check on the liquid analysis and the GasPro GSC analysis. The Poroplot Q and GasPro GSC columns will be switched manually during the course of the run.

Although this revised system will eliminate many of the analytical problems that were encountered during the first run with Cs-promoted "zinc chromite" catalyst, some problems remain unresolved, i.e:

1) Ethane cannot be separated from ethylene; the ethane/ethylene ratio will be estimated based on measured paraffin/olefin ratios for higher carbon number hydrocarbons;

2) Not all of the methanol will condense at -78°C. Therefore, the analysis of the condensed liquid will underestimate the methanol concentration in the reactor effluent;

3) The GC/MS analysis of the condensed liquid, performed in the Chemistry Department, will not be able to distinguish the various isomers of the higher olefins;

4) The GasPro column will not quantify any non-condensed oxygenates that are produced, e.g.; dimethyl ether.

B. February, 1997 Higher Alcohols Run

A run that lasted for about 6 days was carried out during February, 1997 in the continuous stirred autoclave reactor. Decahydronaphthalene (Decalin®, DHN) was the slurry liquid and the catalyst was Engelhard Zn-0312T 1/8 "zinc chromite" promoted with 3 weight percent cesium. This catalyst was operated at the following conditions: temperature - 375°C; total pressure - 2000 psig; space velocity - 5000 sL/Kg. (cat)-hr, and; H_2/CO feed ratio

- 0.5. A 20 wt. % slurry of catalyst in DHN was used, i.e., 16.5 gr. catalyst in 95 mL of DHN.

One change had to be made in the planned analytical procedures, based on the condition of the liquid that was condensed from the effluent gas. These samples had two liquid phases, a light, alcohol-rich phase and a heavy, hydrocarbon-rich phase. The light phase was analyzed in the GC/MS facility of the Chemistry Department and the heavy phase was analyzed off-line using the Poroplot Q column followed by the FID.

Several operating problems occurred during the run that limited the quantity of data that could be obtained, and may influence the interpretation of that data. First, the startup of the run was abnormal. The catalyst was activated according to the normal procedure. However, due to operator error, the catalyst was not exposed to a continuous flow of synthesis gas until about 24 hours after the activation procedure had been completed. During this period, the catalyst was held at 375°C under a gas whose composition was unknown, but probably was very H_2-rich since the last step in the catalyst activation procedure involves a pure H_2 atmosphere.

The second problem was plugging of the condenser that was used to condense the higher-boiling components of the product stream. Plugging was noticed after about 2 days of operation on synthesis gas. The most likely cause is freezing of the slurry liquid, decahydronaphthalene, on the cold surface of the cooling coil. Since the freezing point of DHN is -30°C or -43°C, depending on the isomer, and since the condenser was being operated at a temperature of about -78°C, this is a reasonable hypothesis. As a consequence of this problem, all of the useful data was obtained over a period of about 2 days, before the condenser started to plug.

Finally, when the autoclave was disassembled and inspected after shutdown, there were only about 10 ml of DHN in the reactor, compared to a normal inventory of about 100 ml. Moreover, there was about 100 ml of liquid in the overhead system that had not been returned to the autoclave.

Inspection of the filters that are in front of the metering pump that returns condensate from the overhead system to the autoclave showed that they were clogged with catalyst. Therefore, it is likely that the loss of liquid from the reactor was due to failure of the liquid return from the overhead system.

In view of this problem, plugging of the condenser probably began when liquid DNH that had accumulated in the overhead system was forced through the back-pressure regulator. This suggests that the data obtained during the two days of normal operation were probably not subject to serious uncertainty due to significant liquid loss.

The analysis of the liquid samples is not complete, and analysis of the overall data is still in progress. However, the following preliminary conclusions can be drawn:

1) Olefins, paraffins, methanol and higher alcohols were produced;
2) The quantity of olefins was greater than the quantities of paraffins and alcohols;
3) The amount of *i*-butene produced was greater than the amount of *n*-butene.

C. Thermal Stability of Potential Slurry Liquids

All of the research that has been carried out to date to evaluate the thermal stability of various liquids that might be used as a slurry media for "zinc chromite" catalyst was assembled into a manuscript. This manuscript was submitted to *Industrial and Engineering Chemistry Research* for possible publication. A copy of the manuscript is appended.

D. Paper Presentation at AIChE Spring National Meeting

A paper entitled "The Effect of Liquid Composition on the Performance of "Zinc Chromite" Catalyst in a Slurry Reactor" was presented at the 1997 Spring National Meeting of the American Institute of Engineers (AIChE) on March 12, 1997. This presentation covered the effects of three different slurry

liquids: DHN, tetrahydronaphthalene (THN, tetralin) and tetrahydroquinoline (THQ), on reaction rate and selectivity. No written paper or preprint was prepared.

High-Temperature Slurry Reactors for Synthesis Gas Reactions

I: Liquid Thermal Stability

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ABSTRACT

The use of slurry reactors has been limited to reactions that take place at relatively low-temperatures, less than about 573K, because many of the liquids that have been used to suspend the catalyst are not stable above this temperature. The thermal stability of a number of organic liquids has been evaluated at temperatures between 375 and 425°C and at H_2 partial pressures of about 14 MPa. Saturated and partially-saturated, fused-ring compounds with no alkyl groups or bridges are quite stable at these conditions. Of the compounds tested, tetrahydronaphthalene was the most stable, followed by tetrahydroquinoline and decahydronaphthalene. Analysis of the liquids at the end of the thermal stability evaluation supports some speculation concerning possible reactions leading to degradation.

INTRODUCTION

Alcohols such as isobutanol (2-methyl-1-propanol) and isoamyl alcohol (2-methyl-1-butanol) could be a source of the branched olefins that currently are used to produce octane enhancers such as methyl tertiary butyl ether (MTBE) and tertiary amyl methyl ether (TAME). Over the last decade, there has been a substantial effort to develop technology for producing these alcohols from synthesis gas, a mixture containing carbon monoxide (CO) and hydrogen (H_2). Most research has been carried out in fixed-bed catalytic reactors. A disadvantage of this type of reactor is the mechanical complexity that is required on a commercial scale to remove the heat produced by the highly exothermic alcohol synthesis reactions, and to control the catalyst temperature within acceptable limits (Underwood and Hsiung, 1994). Good temperature control is important to long catalyst life and high selectivity to alcohols.

Slurry reactors may provide a number of advantages for the production of higher alcohols from synthesis gas, including essentially isothermal operation and

rapid heat removal via vaporization and condensation of the slurry liquid. However, selection of an appropriate liquid for the slurry reactor is a critical aspect of process feasibility and performance. The liquid must be compositionally stable at operating conditions, it should not inhibit the reaction, it should have a relatively low vapor pressure, and it should be commercially available at a reasonable cost.

Research on the production of higher alcohols from synthesis gas has been based primarily on two types of catalyst (Forzatti et al., 1991): modified Fischer-Tropsch catalysts and methanol synthesis catalysts promoted with alkali metals. Modified Fischer-Tropsch catalysts produce an Anderson-Schulz-Flory (ASF) product distribution, in which the mole fraction of an alcohol declines monotonically with its carbon number. Methanol is the predominant alcohol and the selectivity to 2-methyl-1-alcohols is low. Therefore, recent attention has been focused primarily on promoted methanol synthesis catalysts.

The starting point for these catalysts is either the "high pressure", "zinc chromite" ($ZnCrO_x$) catalyst or the "low pressure" Cu/ZnO catalyst. Addition of alkali metal promoters such as K and Cs to either of these catalysts shifts the product distribution away from methanol towards C_2^+ alcohols. Depending on operating conditions, both of these catalysts can yield branched alcohols preferentially, among which isobutanol is the main component (e.g., Klier et al., 1984; Tronconi et al., 1995; Minahan and Nagaki, 1995). Large quantities of CO_2 also are formed because both catalysts have high activity for the water-gas-shift reaction.

Promoted $ZnCrO_x$ catalysts have been studied over a temperature range from about 375 to 440°C (e.g., Lietti et al., 1988; Tronconi et al., 1987; Tronconi et al., 1989; Minahan and Nagaki, 1995). This range is essentially the same as that over which the unpromoted catalyst is operated for methanol synthesis (Pasquon and Dente, 1962; Strelzoff, 1970; Stiles, 1977). Promoted Cu/ZnO catalysts operate at about 300 to 325°C (e.g., Klier at al., 1984; Smith and Anderson, 1984; Boz et al., 1994; Underwood

and Hsiung, 1994; Breman et al., 1995). Although high reactor temperatures favor higher-alcohol synthesis, studies of both the unpromoted Cu/ZnO catalyst (Roberts et al., 1993) and a K-promoted Cu/ZnO catalyst (Smith and Anderson, 1984) have shown that deactivation is quite rapid at temperatures approaching 300°C. Moreover, surface area loss of a K-promoted Cu/ZnO catalyst was high at 325°C (Caverly and Anderson, 1987). These results raise the question of whether the stability of Cu/ZnO catalysts will be satisfactory at the higher temperatures required for substantial yields of 2-methyl-1-alcohols.

Synthesis of Alcohols in Slurry Reactor

Fixed-bed reactors are used in all commercial methanol plants. The reaction exotherm is controlled on one of two ways: 1) by using a series of adiabatic reactors with cold gas injection (quench) between reactors (ICI design) (Twigg, 1996) or; 2) by using many small-diameter tubes in parallel, with heat removed through the tube walls (Lurgi design) (Supp, 1973).

In the mid-1970's, a three-phase reactor was developed for methanol synthesis, where the catalyst was suspended in an "inert" hydrocarbon liquid, allowing more efficient heat transfer from both the catalyst particle and the reactor (Sherwin and Frank, 1976). In 1987, a process development unit based on this technology was designed and constructed at La Porte, TX (Studer at al., 1989), and a 260 MTD methanol plant currently is under construction at Kingport, Tennessee (DOE, 1995). A Cu/ZnO catalyst and a high-boiling mineral oil, consisting of either about 100% paraffins or 65% paraffins and 35% naphthenes, were used in most of the research and development leading to this plant (Hsiung et al., 1988; Roberts et al., 1993). Experimentation covered a temperature range from about 235 to 300°C. However, no detailed information on the compositional stability of the mineral oil at these temperatures has been published.

Other research groups have studied methanol synthesis in a slurry reactor, using various Cu/ZnO catalysts and different slurry liquids. Graaf et al. (1988) investigated the kinetics of the reaction using squalane (2,6,10,15,19,23-hexamethyl tetracosane) as the slurry liquid between 210 and 260°C, and von Wedel et al. (1988) studied the kinetics using Vestowax SH 105 at temperatures betweeen 220 and 250°C. The compositional stability of the slurry liquid was not discussed in either case.

The direct conversion of syngas to higher alcohols has been accomplished successfully at both laboratory (Underwood and Hsiung, 1994; Breman et al., 1995) and pilot (Heydorn et al., 1994) scales in a slurry reactor using a cesium-promoted $Cu/ZnO/Al_2O_3$ catalyst at temperatures between 200 to 320 °C. The liquids were a mineral oil containing about 65% paraffins and 35% naphthenes (Heydorn et al., 1994; Underwood and Hsiung, 1994) and *n*-octacosane (Breman et al., 1995). No data was presented on the stability of either liquid at reaction conditions.

Influence of Temperature on Liquid Stability

As noted above, temperatures ranging from 350 to 440 °C may be required for the production of higher alcohols with promoted $ZnCrO_x$ catalyst. Therefore, any liquid to be used in a slurry reactor with this catalyst must be compositionally stable in at least the lower portion of this temperature range. This temperature requirement far exceeds the demonstrated performance of the liquids that have been used with promoted and unpromoted Cu/ZnO catalyst.

In the present work, the thermal stability of nine liquids was evaluated, including two mineral oils (Durasyn® 180 and Drakeol® 34), a naphthenic cut from a petroleum refinery (NB37), and six pure compounds: decahydronaphthalene (DHN, Decalin®), tetrahydronaphthalene (THN, tetralin), perhydrofluorene (PHF), 1,3-di-4-piperidylpropane (134PPDP), decahydroquinoline (DHQ) and tetrahydroquinoline (THQ). The last three liquids, which are basic secondary

amines, were included in this study since they may offer a means to neutralize the intrinsic acidity of the zinc chromite catalyst. The acidity of this catalyst may cause dehydration of higher alcohols to the corresponding olefin and/or dehydration of methanol to dimethyl ether (Tronconi et al., 1987; McCutchen, 1996).

This paper presents data on the thermal stability of these liquids, discusses the reactions that may lead to their degradation, and speculates on the structural features that are associated with liquid stability, or the lack thereof. In Part II, the performance of an unpromoted $ZnCrO_x$ catalyst for methanol synthesis, using three of the most stable liquids, will be reported.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

A thermal stability test (TST) was carried out on each liquid at a standard set of operating conditions to determine the extent to which the liquid is thermally stable in the absence of catalyst, and the products formed when the liquid degrades. The test was conducted in a 300 cm^3 stirred autoclave made of 316 stainless steel, with H_2 continuously bubbling through the liquid. The gas leaving the autoclave passed into a gas/liquid separator containing an internal cooling coil with tap water as the cooling medium. The condensed liquid was returned continuously to the autoclave with a metering pump. The uncondensed gas passed through a back-pressure regulator to an analytical system, as described below.

The standard operating conditions for the TST were: autoclave temperature - 375 °C; total pressure - 1000 psig; H_2 flowrate - 3.5 sL/min; initial volume of liquid - 150 ml. The test was continued for 72 hours once the autoclave reached the specified temperature. High-purity H_2 (99+ mole %) was used, and the flow rate was measured and controlled with a mass flowmeter. The program for heating the autoclave was as follows: ambient to 200 °C in 1 hr; 200 to 300 °C in 2 hrs; 300 to 375 °C in 5 hrs; hold at 375 °C for 72 hrs, and; cool from 375 °C to ambient in 5 hrs. The

gas/liquid separator temperature was held at 25°C in order to condense most of the liquid that vaporized and left the autoclave with the gas stream. Liquids were used as received from the supplier, without further purification.

The composition and flow rate of the gas leaving the autoclave were measured periodically during the experiment. The gas was analyzed using a Perkin-Elmer Autosystem gas chromatograph with thermal conductivity (TCD) and flame ionization (FID) detectors, with argon carrier gas used for each detector. The permanent gases, CO, CO_2, H_2, N_2, and H_2O, were analyzed with a 1.5 m long, 3.2 mm diameter stainless-steel Carboxen 1000 packed column which was connected to the TCD. Hydrocarbons were analyzed with a 30 meter, 0.032 mm diameter Poroplot Q capillary column which was connected to the FID. Process samples were taken on-line with a gas sampling valve equipped with two gas sample loops, each dedicated to a column/detector combination.

The gas chromatographic data was recorded and stored by Turbochrom 3, a PE Nelson software package which ran on a IBM 386 personal computer. The software allowed for automated sampling and identification of peaks and the sample composition, as long as standards had been stored in the software database. Gas standards of mixtures with known concentrations were typically run before every TST.

The flow rate of the gas leaving the autoclave was measured with a Precision Scientific wet test meter. The meter was filled with high boiling Drakeol® 10B mineral oil since the autoclave exit gas was heated above 100°C to prevent product condensation.

At the conclusion of each TST, the reactor was opened and the remaining liquid was carefully collected, weighed and analyzed. Analyses included molecular weight by vapor pressure osmometry (VPO), density, refractive index, nuclear

magnetic resonance (NMR) spectroscopy and gas chromatography/mass spectrometry (GC/MS).

Liquid Analysis

PONA Analysis

The PONA (Paraffin, Olefin, Naphthene, Aromatic) analysis is a common method used to characterize complex mixtures of hydrocarbons, such as mineral oils, naphthas, kerosenes and other petroleum fractions (Van Nes, 1951). For high-molecular-weight hydrocarbon mixtures, such as Drakeol 34 and Durasyn 180, PONA analysis was accomplished with the n-d-M method (ASTM D1480-91; 1994). This method applies to olefin-free petroleum fractions and requires measured values of the refractive index (n), density (d) and molecular weight (M) of the fraction. With this data, the average number of aromatic rings (Ra) and naphthenic rings (Rn) in a hypothetical mean molecule can be calculated, and the liquid composition can be expressed in terms of a carbon distribution, i.e., the percentage of the total number of carbon atoms present in aromatic ring structures (% A), naphthenic ring structures (% N) and in paraffin chains (% P).

The data required for this method was obtained as follows: 1) refractive index was measured using an Abbe refractometer; 2) density was measured by an outside laboratory (ASTM D1480-91; 1994), and; 3) molecular weight was determined by an outside laboratory (ASTM D 2502-82; 1994).

NMR Analysis

Many of the liquids were analyzed using ^{1}H and ^{13}C NMR. The clearest results were obtained from ^{13}C NMR. However, ^{1}H NMR allowed the ^{13}C spectra to be verified, especially in the case of pure liquids (e.g., DHN, DHQ, THQ, THQ and PHF). NMR measurements were carried out using a General Electric OMEGA 300

MHz instrument with proton and carbon frequencies of 300.52 and 75.57 MHz respectively, using H-C dual probe in a 5 mm tube. Inverse-gated decoupling, in which decoupling was on during data acquisition and was gated off during the relaxation delay between pulses, was employed for the carbon measurement to see decoupling effects only. An exponential multiplication with line broadening of 3-5 Hz was applied to the carbon spectra after 512 transients to improve the signal-to-noise ratio without any noticable degradation in the resolution. Sixty-four transients were acquired for the proton spectra and no apodization was applied.

Identification of components or structural groups in a molecule was done by comparison with the NMR spectra of pure components (Silverstein et al., 1991; Pouchert and Behke, 1993).

GC/MS Analysis

Gas chromatography/mass spectrometry (GC/MS) was also used to analyze many of the liquids. GC/MS analyses were carried out using a Hewlett-Packard 5985B quadrupole mass spectrometer and an RTE-IV data system. The column was a 30 m fused silica capillary column (J & W Scientific) 0.32 mm in diameter with a 10 μm film thickness. The temperature program began with a two-minute hold at 60°C, followed by a ramp of 10 degrees per minute to a final temperature of 270°C. The injector and transfer line were at 300°C. One microliter of sample was injected splitless with a split time of 1 minute. The mass spectrometer was operated with 70 eV electron ionization. The mass range scanned was 40 to 400 daltons.

In the tables that follow, the "retention time" is the time required for a component to pass through the gas chromatograph, where the components are separated prior to entering the mass spectrometer. The "probability (%)" was determined in the following manner. For each peak detected, the mass spectrometer analyzer provides a list of the most probable structures, by comparing

the unknown to a library data base of 78,000 known compounds. The "probability" is based on how well the unknown and library structure compare. A match with greater than 80% probability is considered excellent. In these tables, the component with the highest probability has been selected for each peak. However, structural isomers are often difficult to distinguish due to similarities in their spectra.

Additional details concerning equipment and procedure are provided by Márquez (1996) and McCutchen (1996).

RESULTS

Liquid Characteristics

Table 1 presents the major properties of the nine liquids that were studied. Figure 1 shows the structures of the six pure compounds.

Table 2 summarizes some of the main results obtained in the TSTs. Several items merit some explanation:

1) Initial weight of liquid charged to reactor: The normal charge was 150 ml. For DHQ, 134PPDP and NB37, only about 100 ml were used. An estimate of the density of decahydronaphthalene at 375°C showed that this liquid expands by about a factor of about 2 between 20°C and 375°C. An expansion of this magnitude would make the volume of liquid at 375°C close to the working capacity of the autoclave, even before allowing for gas holdup. Therefore, it is possible that some small loss of liquid resulted from physical carryover through the overhead system and back-pressure regulator in some of the experiments.

2) Rate of C_1-C_4 gas production: This rate was calculated using the measured gas outlet compositions and effluent gas flowrates. Two values are presented: a) the maximum rate of gas production, which usually occured during the first few hours of the test, close to the time at which the steady-state operating temperature was reached, and; b) the steady-state rate of gas production, which represents the average

rate of gas production once this rate had stabilized, usually after about one day of operation.

3) Rate of liquid loss via C_1-C_4 gases (maximum or steady state):

$$= \frac{\text{Rate of } C_1 - C_4 \text{ gases produced / hr (maximum or steady state)} * 100}{\text{initial weight of liquid charged}}$$

4) Total weight of liquid lost (% of initial charge):

$$= (1 - \frac{\text{weight of liquid remaining in autoclave after 72 hr}}{\text{initial weight of liquid charged}}) * 100$$

Table 2 shows that the amount of C_1-C_4 gases produced generally was a small fraction of the liquid lost during the TST. Some other, unquantified sources of liquid loss include: liquid vaporization, i.e., liquid in the exit gas corresponding to the pure component vapor pressure of the liquid at the temperature of the overhead system; decomposition of the liquid to C_4^+ species not condensed in the overhead system; liquid handling when the reactor was discharged, and; liquid remaining in the reactor and the overhead system.

Stability of Individual Liquids

Durasyn 180

Table 2 shows that Durasyn 180 exhibited the highest C_1-C_4 gas production and the highest liquid loss rates of all nine liquids. Table 3 shows that there was an 86% reduction in molecular weight, from a measured value of 1449 to 198, and that the appearance of the liquid changed markedly, from colorless and very viscous to yellow and non-viscous after the TST. These data suggest significant decomposition. Table 3 also contains the n-d-M data and the carbon distribution calculated from these data. The percent of cyclic, i.e., aromatic (A) plus naphthenic (N), carbons increased from 7 to 18 % during the TST, and the paraffinic carbons

decreased from 93 to 82 %. This suggests some dehydrocyclization and/or preferential cracking of the paraffinic structures.

Figure 2 presents a comparison of the ^{13}C NMR spectra for the fresh and spent samples, in the spectral region from 10 to 50 ppm where most of the peaks are located. Recall that Durasyn 180 is a hydrogenated homopolymer of 1-decene, comprising a mixture of C_{40}, C_{50}, C_{60} and C_{70} paraffins, and is highly branched. Most of the branches are C_8 groups. Some features of the spectra of the fresh sample are similar to these of octane and higher paraffins, reflecting the linear portions of the molecules. These features are single peaks in the regions of 14-15, 22-24 and 32-33 ppm, and a triplet at 29-31 ppm. The other peaks in the region of 27 and 37-39 ppm correspond to the branches of the molecule.

Comparison of the two spectra in Figure 2 indicates that: 1) the peaks in the regions of 26-29 and 34-44 ppm are higher in the fresh sample than in the spent, indicating more branching in the fresh sample; 2) the peaks at 30.7 and 31.3 are diminished in the spent sample, indicating that the chains are shorter; 3) there is a slight increase in the peak at 32.5 ppm in the spent sample, indicating less branching in the spent sample, and; 4) there is a doublet in the spent sample at 29-31 ppm instead a triplet. This doublet is found in structures such as heptadecane and larger linear paraffins, whereas the triplet is associated with shorter linear paraffins such as octane. Again, the loss of branches in the spent liquid is indicated. Overall, these changes in the NMR spectra suggest that the spent liquid has longer linear segments and fewer branches.

The region of 80-140 ppm was enlarged with respect to the solvent peak, deuterated chloroform ($CDCl_3$), at 77 ppm, and is presented in Figure 3. Traces of aromatics, corresponding to the small peaks at 124 to 128 ppm, are present in the spent sample. This is consistent with the increase in the aromatic content of the spent sample reported in Table 3.

Based on the collective data, it appears that Durasyn 180 was thermally hydrocracked, reducing significantly molecular weight and the branching of the molecules. Alkyl branches either left the original molecule as volatile gases or stayed in the liquid as molecules with lower molecular weight. The results of this test suggest that branching in hydrocarbons is detrimental to liquid stability. It is interesting to note that the final molecular weight of the "spent" Durasyn (198) was roughly comparable to the molecular weight of the monomeric units in fresh Durasyn (142), suggesting that hydrocracking of the longest alkyl groups at tertiary carbons may have been a primary mechanism of degradation.

Drakeol 34

Drakeol 34 is similar in composition to the liquid that has been used to slurry Cu/ZnO catalysts at lower temperatures (Hsiung et al., 1988; Studer et al., 1989; Roberts et al., 1993). Table 2 shows that the amount of liquid lost during the TST was the second highest of all the liquids. The maximum and steady-state rates of C_1-C_4 gas production were somewhat lower than those of Durasyn 180, but still very high compared to most of the other liquids tested. Table 4 contains various analyses of liquid composition for the fresh and spent liquids. The molecular weight decreased by 35%, from a measured value of 405 to 264, and the appearance of the liquid changed from colorless and viscous to yellow and non-viscous. The percentage of carbon atoms in cyclic compounds, primarily naphthenes, increased from 35 to 40 %. However, the average number of rings per molecule declined from 2 for the fresh liquid to 1.3 for the spent sample.

Figure 4 presents a comparison of the ^{13}C NMR spectra for fresh and spent Drakeol 34 in the region from 5 to 50 ppm. Several features should be noted: 1) the peaks at 14.1, 23 and 32.5 ppm have increased in the spent sample; 2) the triplet at 30 ppm has become a doublet, and; 3) the peaks at 20.3, 33.2 and 37.5-38.5 ppm have

decreased. Moreover, a comparison of the NMR spectra for fresh Drakeol 34 with that of pure decahydronaphthalene (Pouchert and Behke, 1993) leads to the conclusion that Drakeol 34 does not contain any significant concentration of fused rings, since peaks at 36.4 and 43.6, corresponding to the two carbons that are common to both rings in DHN, do not appear in the Drakeol 34 spectra. As with Durasyn 180, the NMR spectrum of Drakeol 34 in the region of 128-132 ppm showed traces of aromatics in the spent liquid that were not present in the fresh sample.

On balance, the NMR results indicate that the paraffinic molecules in Drakeol 34 became less branched and shorter over the course of the TST. The loss of branching is shown by the decrease in the peaks at 20.3, 33.2 and 37.5-38.5 ppm, and by the transformation of the triplet at 30-31 ppm into a doublet. The shorter linear segments are suggested by the increased peaks at 14.1, 23 and 32.5 ppm.

The major changes that occurred during the TST were molecular weight reduction, production of light gases, loss of branching, an increase in the percentage of cyclic carbons, a reduction in the average number of rings per molecule and an increase in the concentration of shorter paraffinic segments. These features can be rationalized through two types of hydrocracking reaction, i.e., scission of C-C bonds followed by hydrogenation of unsaturated terminal carbons resulting from the scission. These two reactions are shown in Figure 5.

The hypothetical molecule on the left-hand side of Reaction A represents a generalized saturate with one branch on the backbone. Since the initial average molecular weight of Drakeol 34 is 405, the number of carbons in an average molecule is about 29, i.e., $n+m+p \equiv 25$. Moreover, on average, there are two naphthenic rings in the molecule. Given that Drakeol 34 is completely saturated, the parameters x, y and z are bounded by +1 and -(number of naphthenic rings in segment). For example, if $x = +1$, the segment C_nH_{2n+1} is totally paraffinic. If $x = -1$, the segment C_nH_{2n-1} must be a naphthene ring, e.g., C_5H_9 or C_6H_{11}, and if $x = -3$, the

segment C_nH_{2n-3} consists of three, non-fused naphthene rings. Intermediate values of x represent segments that contain both paraffinic and naphthenic elements.

Reaction A, which shows hydrocracking between secondary and tertiary carbons, can account for the reduction in branching that was observed, as well as some of the reduction in molecular weight. Moreover, if the smaller of the two product molecules has a carbon number below about 8, it may leave the reactor as a gas, contributing to the loss of liquid. To the extent that paraffinic carbons leave the reactor as light gases, this reaction also can account for the increase in the fraction of naphthenic carbons. Moreover, if each of the product molecules contains at least one naphthene ring, this reaction leads to a reduction in the average number of rings per molecule.

Reaction B shows hydrocracking between two secondary carbons, or between a primary carbon and a secondary carbon. Reaction B also can contribute to molecular weight reduction, to gas production, and to loss of liquid. Reaction B also can account for the observed reduction in the average number of rings per molecule, again providing that each of the product molecules contains one or more naphthene rings. However, Reaction B does not contribute to a reduction in branching, and may, in fact, lead to increased branching if an unbranched product molecule leaves the autoclave as a gas.

Decahydronaphthalene (DHN)

As shown in Table 2, DHN exhibited one of the lowest C_1-C_4 gas production rates, 0.095 wt %/hr of the initial charge as a maximum and 0.0040 %/hr at steady state. The loss of weight at the end of the TST was 26%.

Figure 6 presents ^{13}C NMR spectra for the fresh and spent samples. The DHN used in this test contained approximately 64 mole% of the trans isomer and 36% of the cis, the spectra for the fresh sample was essentially identical to the spectra for

that mixture (Pouchert and Behke, 1993). Both the fresh and spent samples had similar spectra. The most significant difference was an increase in the peak at 36.4 ppm in the spent sample, indicating that some trans- to cis- isomerization took place. This conclusion is supported by the appearance of very small humps at 24 and 29 ppm in the spent sample, which belong to the cis compound. However, the trans peaks at about 34.5 and 44 ppm still dominate the spectrum. No peaks were observed other than those of the DHN isomers.

GC/MS analysis was carried out on both fresh and spent samples. According to the results in Tables 5 and 6, the DHN changed from 64% trans/36% cis to 61% trans/39% cis over the course of the TST, a small change which qualitatively is consistent with the NMR results. No other compounds were detected in the spent sample.

The excellent thermal stability of DHN shown by the NMR and GC/MS analyses is somewhat inconsistent with the 26% loss of liquid over the course of the TST. If DHN were hydrocracked, the most likely products would be C_1-C_4 gases and C_6-C_{10} components, as illustrated in Figure 7. If such decompositions took place to the extent of 26 wt % of the initial liquid charge, much larger concentrations of C_1-C_4 hydrocarbons would have been detected in the effluent gas, and single ring products, e.g., butyl cyclohexane, methyl cyclohexane and cyclohexane, would have been detected in the spent liquid. Complete evaporation of the alkyl cyclohexanes from the autoclave is unlikely in view of the low temperature at which the overhead system was operated. For example, the boiling point of butyl cyclohexane is 181 °C and the boiling point of methyl cyclohexane is 101°C. These are sufficiently high that complete loss of alkyl cyclohexanes from the spent liquid seems unlikely. Therefore, some of the other sources of liquid loss, as mentioned earlier, probably were operative in this experiment.

Perhydrofluorene (PHF)

As shown in Table 2, PHF had the lowest liquid loss, 9 wt %, of any of the liquids tested. However, the rates of C_1-C_4 gas production, 0.44 wt % of the initial charge/hr (maximum) and 0.044 wt % of the initial charge/hr (steady state) were five to ten times that of DHN.

Figure 8 shows ^{13}C NMR spectra for fresh and spent PHF samples. Naphthenic carbons generally appear in the region of 24 to 55 ppm. All of the peaks for the fresh sample lie in that region. A large number of new peaks appeared as a result of thermal treatment, indicating the formation of a complex mixture. Two of the newly-formed peaks were outside of the naphthenic range. The peak at 15 ppm suggests alkyl chains attached to a naphthenic ring. Moreover, the very small peaks at 124-128 ppm show that traces of aromatics were present in the spent sample. Both benzene and toluene signals are present in this region.

The complicated mixture of products in the PHF spent sample was confirmed by GC/MS analysis, as presented in Table 7. Although this data indicates that there was no measurable net reduction in molecular weight, PHF did undergo some significant reactions. Six compounds with the same molecular weight as PHF were detected, accounting for 49.2 mol% of the spent sample. These compounds may be either cis-trans isomers or isomers in which one of the terminal cyclohexyl groups has rearranged to a methyl cyclopentyl group. Three compounds with a molecular weight of 180 were also detected, accounting for 6.2 mol% of the spent liquid. These compounds may have resulted from hydrocracking of a C-C bond in one of the rings to give a $C_{13}H_{24}$ compound such as those shown in Figure 9. The last three of these compounds could account for the NMR signal at 15 ppm.

The remaining compounds in Table 7 constitute a minor portion of the spent liquid, but their presence suggests the possibility of ring-opening reactions followed

by dealkylation. The possibility of unsaturation in both the rings and the pendant groups also is suggested.

On balance, PHF was much more stable than Drakeol 34 and Durasyn 180, but not as stable as DHN. This suggests that either separation of the two cyclohexane rings by a cyclopentane ring, or simply the increase in the total number of rings and/or C-C bonds, could have decreased the stability of the molecule.

Decahydroquinoline (DHQ)

Decahydroquinoline (DHQ) is a secondary amine, having cis- and trans-isomers. The commercially-available liquid is trans-DHQ, which was used in this test. Cis-DHQ is a solid at ambient temperature, with a melting point of 40 °C. Table 2 shows a 31 wt % liquid loss and relatively high rates of C_1-C_4 gas production, 0.066 wt % of the initial charge/hr (steady state) and 0.17 wt %/hr (maximum). The appearance of the liquid changed significantly during the TST, from clear and colorless to brown and semi-waxy, with a very strong smell.

NMR and GC/MS analyses showed that isomerization of trans-DHQ to cis-DHQ took place during the TST. Figure 10 shows the ^{13}C NMR spectra for the fresh and spent samples. The main changes in the spectra were: 1) increases of the peaks in the regions of 20-33 and 43-47 ppm and at 62 ppm, and; 2) decreases in the peaks at 35 and 53 ppm. These changes result primarily from an increase in the concentration of cis-DHQ and a corresponding decrease in the concentration of trans-DHQ. The new peaks formed in the region of 120-160 ppm suggest tetrahydroquinoline (THQ), formed by complete dehydrogenation of one of the rings of DHQ.

Table 8 presents the estimated composition and molecular weight for the spent sample based on GC/MS analysis. The spent liquid contains 83% trans- and 11% cis-DHQ, the latter providing a waxy characteristic to the final product. The

observed formation of cis-DHQ is, of course, consistent with the NMR results. A minor amount, i.e., 6 %, of other compounds was observed. About 1% of THQ was detected, again consistent with the NMR results. Hydrocracking of a ring at either a C-C bond or a C-N bond gives a product of molecular weight 141, which accounts for 3.2 mol% of the spent sample. The other two trace components (1.4 mol%) are difficult to rationalize; the even molecular weight suggests loss of nitrogen from the structure.

1,3-Di-4 Pyperidylpropane (134PPDP)

This compound is a white, odorless solid at ambient temperature with a melting point of 67.1°C. The material remaining in the autoclave after the TST was a black liquid at ambient temperature with a very strong smell. The weight of liquid recovered at the end of the TST was 30 % less than the original charge, as shown in Table 2. The rate of C_1-C_4 hydrocarbon production was relatively low, 0.22 wt % of the initial charge/hr (maximum) and 0.002 wt %/hr (steady state).

Table 9 shows that the spent liquid is a mixture of compounds with molecular weights ranging from 93 to 205, with an average of 154, corresponding to a 27% reduction in molecular weight. The product mixture is so complex, and some of the identifications are sufficiently tenuous, that it is important to note that the components identified in the GC/MS analysis have not been confirmed by analysis of standards, and it is possible that the actual components could be isomeric forms of those named. For example, the compound identified as ethyl pyridene could be dimethyl pyridene instead. It is interesting to note that there was no detectable concentration of 134PPDP in the spent sample, which shows that PPDP is completely cracked at these temperatures. The GC/MS results suggest that the main 134PPDP decomposition pathway is through cracking in the alkyl (propyl) bridge that connects the two piperidine rings, accompanied by dehydrogenation of the various

piperidines to pyridines. Four compounds, constituting about 25 mol% of the spent liquid, are consistent with this pathway. About 25 wt % of the liquid at the end of the TST was composed of compounds that did not contain nitrogen, suggesting that thermal hydrodenitrogenation of the rings in 134PPDP is relatively facile. Cleavage of one of the piperidene rings along with dehydrogenation of the other can explain the presence of three compounds, constituting about 16 mol% of the spent liquid.

Naphthenic Base 37 (NB37)

NB 37, a naphthenic cut from crude oil distillation, is used to produce lubricants and is a commercial product from the Amuay refinery in Venezuela, owned by Lagoven, an affiliate of Petroleos de Venezuela S.A. Table 10 presents some of the properties of this liquid.

The results in Table 2 indicate that NB37 is not very stable at the conditions of the TST. The appearance of the liquid changed from clear and colorless to brown over the course of the test. A 41 wt % liquid loss was observed, along with the highest steady-state C_1-C_4 gas production, 0.13 wt % of the initial charge/hr. This is comparable with that of Durasyn 180 and two orders of magnitude higher than that of DHN.

Vapor pressure osmometry (VPO) measurements indicated a molecular weight reduction of only 4 %, from 300 to 288. Due to the complex composition of NB37, NMR and GC/MS analyses were not carried out.

Tetrahydronaphthalene (THN, tetralin)

THN exhibited one of the best liquid recoveries. The weight lost at the end of the TST was 13 wt%, half of the DHN loss, and slightly greater than the 9 wt% loss of PHF. The appearance of THN changed from colorless to orange-maroon. The

production rate of C_1-C_4 gases was very low; both the maximum and steady-state gas production rates were well below those of any other liquid, as shown in Table 2.

GC/MS results for the spent liquid sample are presented in Table 11. THN constituted approximately 96 wt% of the sample, and there was no reduction of molecular weight. The remaining 4 wt% of the liquid was a compound with the same molecular weight as THN, identified as 2,3-dihydro-1-methyl indene. The absence of 2,3-dihydro indene in the spent sample suggests that demethylation of 2,3-dihydro-1-methyl indene is relatively slow.

Due to these encouraging results, another TST was carried out at a higher temperature, 425°C, at otherwise identical conditions. The liquid loss was 10 wt % at 425°C versus 13 wt % at 375°C. However, the GC/MS analyses presented in Table 12 indicated some significant changes in the liquid composition. The concentration of THN in the spent liquid was only 42 wt %. The remaining components were: 1) 2,3-dihydro-1-methyl indene; this was the next largest component (33 mole %) and was also observed in the test at 375°C; 2) molecules that probably resulted from opening of the saturated ring, i.e., butyl benzene (18 mole %) and methyl propyl benzene (1 mole %); 3) products that may have resulted from hydrocracking of the alkyl groups resulting from ring opening, e.g., toluene (1 wt %) and ethyl benzene (2 wt %), and; 4) naphthalene (3 wt %), formed by dehydrogenation of THN.

The average molecular weight did not change significantly; there was a 1 % reduction from 132 to 131. However, the presence of 22 mole % alkyl benzenes shows that the saturated ring in THN had some tendency to open at 425°C. No 2,3 dihydroindene was observed, again suggesting that the methyl group in 1-methyl-2,3- dihydroindene is not easily removed, even at 425°C.

Figure 11 shows some reactions that may account for the major products formed from THN at 425°C. Opening of the saturated ring takes place in all these

reactions. Some reactions involve the release of gaseous species, such as ethane and propane, consistent with the increased gas production rates shown in Table 2.

Tetrahydroquinoline (THQ)

The weight of liquid lost in the TST was the lowest of all the liquids, 9 wt %, as shown in Table 2. The appearance of the liquid changed from pale yellow to orange-maroon. The production rate of C_1-C_4 gases was low, less than that of DHQ at steady state, but greater than those of DHN and THN. GC/MS results, presented in Table 13, indicate that 75 mole % of the spent liquid was THQ. The second largest component, 9 mole %, was 5,6,7,8 THQ. This is an isomer of THQ with the nitrogen atom in the aromatic ring, as shown in Figure 12. The other significant product was quinoline (7 wt %), formed by dehydrogenation of THQ. There also was a small amount (1 mole %) of decahydroquinoline, formed by hydrogenation of the aromatic ring. These three products, plus THQ itself, accounted for 93 mole % of the spent liquid. The small concentration of THN probably resulted from contamination from a previous run.

There was some formation of products that probably resulted from opening of the saturated ring in THN, followed by hydrocracking of the alkyl group, i.e., methyl and ethyl benzamine (<2 mol%). Despite the low molecular weight of these compounds, the average molecular weight of the liquid did not change during the TST. This is because some species with molecular weights higher than THQ were formed. Except in the case of ethyl quinoline, these higher-molecular-weight compounds could not be identified definitively. However, the unknown heavy compounds have molecular weights of either 147 or 161. The former might correspond to methyl THQ and the latter to ethyl or dimethyl THQ. Although the high-molecular-weight compounds comprise only about 4 mole % of the spent

THQ, the possibility of alkylation is of potential importance in an actual reacting system.

Figure 12 shows some of the possible reactions that could lead to the major products formed in the THQ TST at 375°C.

DISCUSSION OF RESULTS

This research appears to be unique in that the decomposition of various organic compounds was studied in the presence of high partial pressures of H_2. However, the results are consistent qualitatively with research on similar compounds in the absence of H_2, as discussed below.

The effect of molecular structure on thermal stability has been studied by several investigators. For example, factors such as chain length and chain branching of paraffinic hydrocarbons were evaluated to estimate the high temperature limit of synthetic oils for aviation applications (Koch, 1990). Tests were carried out with different types of liquids in order to establish their stability at 370°C. The hydrocarbons tested were: hexadecane, hexamethyltetracosane (squalane) and various polyalphaolefins (PAO), i.e., hydrogenated decene oligomers. The structures of squalene and PAO trimer are shown in Figure 13. The PAOs were denoted as PAO-1 through -5. PAO-1 and -2 were primarily the dimer, with small concentrations of trimer. PAO-3 and -4 were primarily the trimer, with small concentrations of tetramer, and PAO-5 was approximately a 1/3 mixture of trimer and tetramer. The degree of branching, e.g., the number of tertiary carbon atoms in the molecule, increases with the number of monomers.

The tests were carried out by loading 1 ml of sample into an O_2-free chamber, heating to 370°C and holding at this temperature for times between 1 and 6 hrs. The stability of the liquid was evaluated based on: viscosity change, increase of pressure due to liquid decomposition, and the amount of the starting compound remaining

after the test. The products of decomposition were not identified. The overall order of thermal stability was: hexadecane > PAO-1 ~ PAO-2 > squalane > PAO-3 ~ PAO-4 > PAO-5, leading to the conclusions that: 1) linear (non-branched) paraffins have better thermal stability than branched paraffins; 2) within the series of PAO's, PAO-1 and -2 were the most stable, PAO-3, and -4 were intermediate and PAO-5 was the least stable, suggesting a negative effect of branching, i.e., the number of tertiary carbon atoms, on thermal stability, and; 3) the length of the group attached to a tertiary carbon atom adversely affects thermal stability. Squalene (a C_{30}) contains six tertiary carbon atoms, each with a methyl group attached. The less-stable PAO trimer (also a C_{30}) contains only two tertiary carbons, but each has a C_8 alkyl group attached.

Fabuss et al. (1964) investigated the thermal decomposition rates of a number of saturated mono-, bi- and tri-cyclic hydrocarbons. The products of decomposition were not identified; only the rate of disappearance of the original compound was measured. Tests were run over a temperature range from 371 to 455°C. The authors presented a correlation of the first-order decomposition rate constant at 427°C against a parameter based on molecuar structure. This correlation leads to the conclusions that the decomposition rate increases with: 1) the presence and length of alkyl groups on the rings; 2) the number of rings in a fused-ring structure, and ; 3) the presence of alkyl bridges between saturated rings. It also suggests that molecules containing a methyl group are much more stable than those containing a longer alkyl group.

Fabuss et al. (1964) also determined that the activation energy for decahydronaphthalene decompostion was about 64 Kcal/mole, leading to a decomposition rate constant at 375°C of about 0.001 hr^{-1}. Using this rate constant, a fractional decahydronaphthalene decomposition of about 8% can be calculated over

the duration of the TST. This result is consistent qualitatively with the experimental data for DHN shown above.

The correlation of structure with decomposition rate presented by Fabuss et al. is also consistent with several of the observations made during this research. For example, the high rate of decomposition of 134PPDP may be attributable to the presence of a propyl bridge between two piperidene rings, and the decrease in the average number of naphthenic rings per molecule of Drakeol mineral oil may be the result of alkyl bridges between saturated rings. Moreover, the increase in the ratio of naphthenic carbons to paraffinic carbons in Drakeol may be attributable in part to dealkylation of alkyl naphthenes.

Humberg and Savage (1996) studied the pyrolysis of 9-n-dodecylperhydroanthracene (DDPA) at temperatures between 400 and 450°C in the absence of added H_2. They found that the primary reaction products were produced either by breaking of the C-C bond that joins the alkyl group to the ring, or by breaking the immediately adjacent C-C bond in the alkyl group. Ring-opening reactions were relatively unimportant. Humberg and Savage rationalized their results in terms of a free-radical mechanism involving H abstraction followed by β–scission. The predominant product pair was found to result from H abstraction from a tertiary carbon, the weakest C-H bond in the DDPA molecule, followed by scission of the weakest C-C bond, that joining the alkyl group to the ring. The relative unimportance of ring-opening reactions was hypothesized to result from a "pseudo cage effect", which permits closing of an opened ring due to the close proximity of the reactive ends.

The same mechanistic arguments can help to explain some of the present results, as well as the results of Koch (1990). For example, the tendency of Durasyn 180 to become less branched might be attributed to the relative ease of H abstraction from a tertiary carbon, the tendency of Drakeol 34 to become more naphthenic

might be attributed to the ease of dealkylation relative to ring opening, and the relative instability of PHF might be attributed to the presence of twice the number of tertiary carbons and a larger number of relatively weak tertiary/tertiary and tertiary/secondary C-C bonds, relative to decahydronaphthalene. This mechanistic picture also accounts for the lower stability of alkylated saturated cyclic hydrocarbons, as opposed to their unalkylated counterparts, as observed by Fabuss et al., and the relative stability of methylated saturated rings, also observed by Fabuss et al. (1964) and suggested by some of the present results, e.g., the relative stability of dihydromethylindene.

CONCLUSIONS

This research has shown that several hydrocarbon liquids are compositionally stable at 375°C and 7.0 MPa of H_2 partial pressure, in the absence of a catalyst. The three most stable liquids: decahydronaphthalene, tetrahydronaphthalene and tetrahydroquinoline, have been tested for methanol synthesis in a slurry reactor at temperatures of 325°C and 375°C and at a total pressure of 13.9 MPa, using a commercial "zinc chromite" catalyst and a feed consisting of a mixture of H_2 and CO. The results will be reported separately.

The present results, combined with earlier studies of neat hydrocarbon pyrolysis, permit some speculation concerning the stability of various molecularstructures. Compounds that contain fused six-membered rings with no alkyl groups appear to have exceptional stability, as suggested by studies in the absence of H_2 (Fabuss et al., 1964). Paraffins, especially branched paraffins, appear to be much less stable. Alkyl groups or alkyl bridges in naphthenic molecules appear to reduce overall stability.

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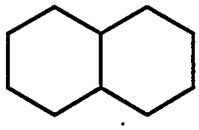
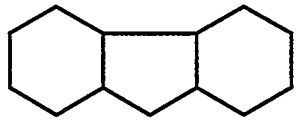
List of Figures

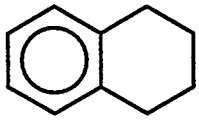
Figure 1. Chemical structures of the pure liquids



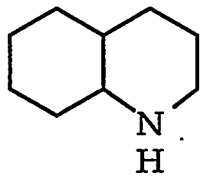
Decahydronaphthalene
(DHN)



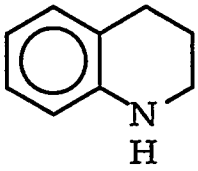
Perhydrofluorene
(PHF)



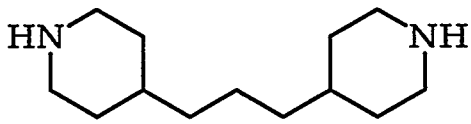
Tetrahydronaphthalene
(THN)



Decahydroquinoline
(DHQ)



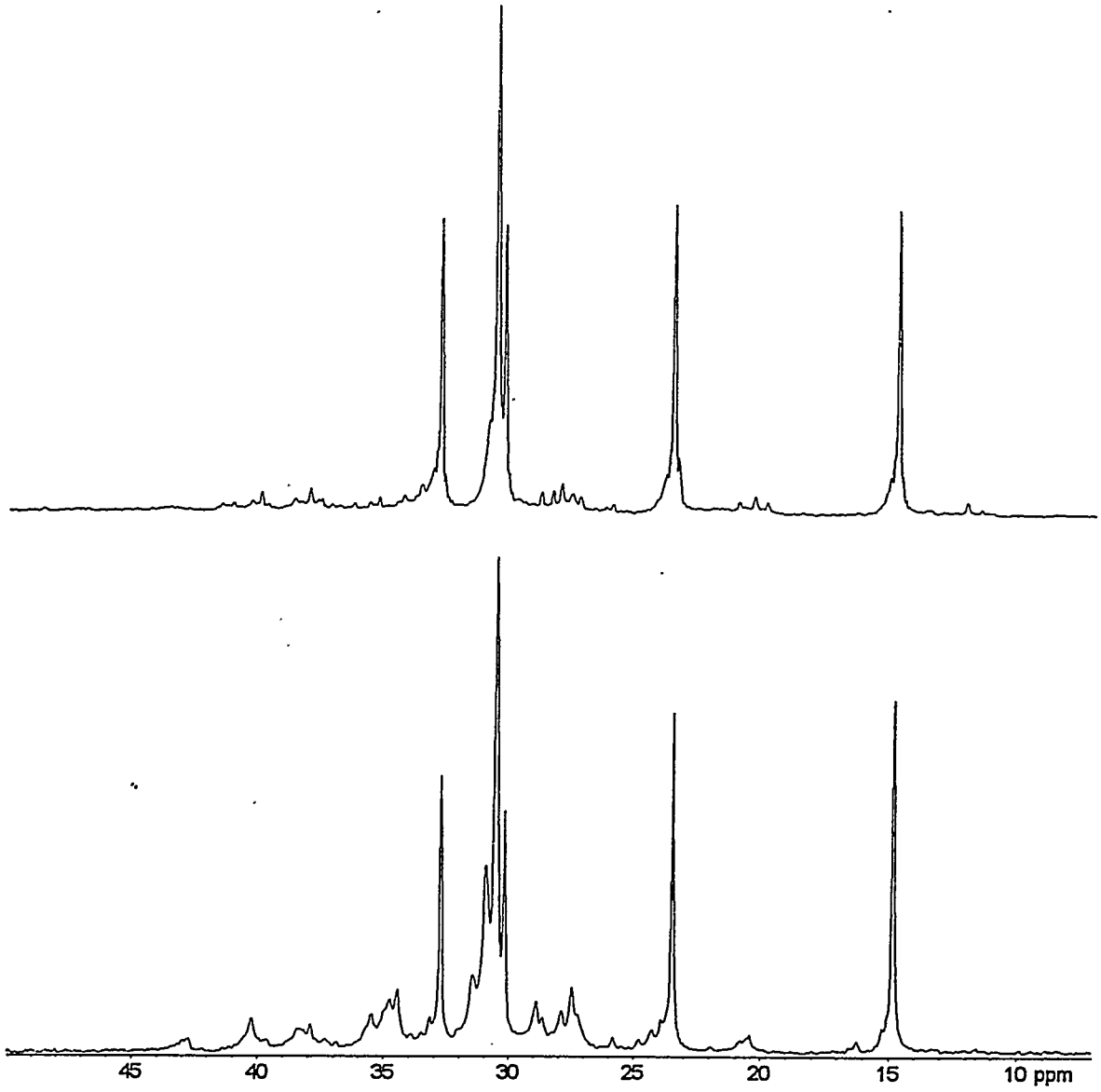
Tetrahydroquinoline
(THQ)



1,3-Di-4 Pyperidylpropane
(134PPDP)

Fig. 2

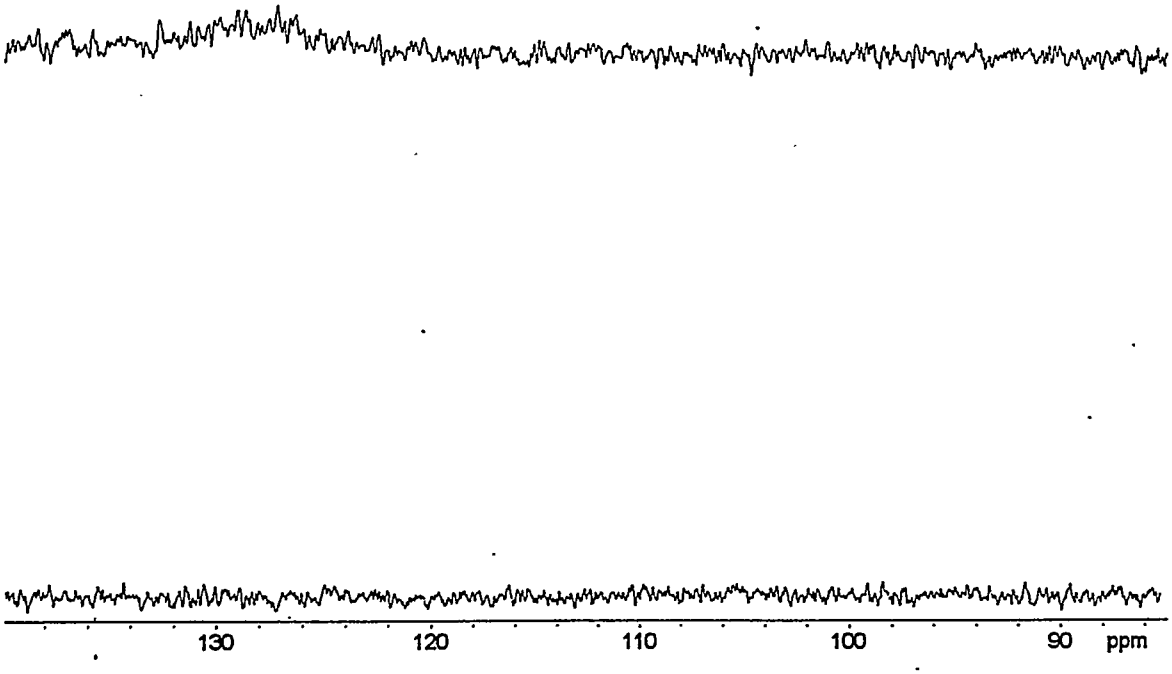
DURSC.DAT (7-50 PPM)



DURFC.DAT (7-50 PPM)

Fig. 3

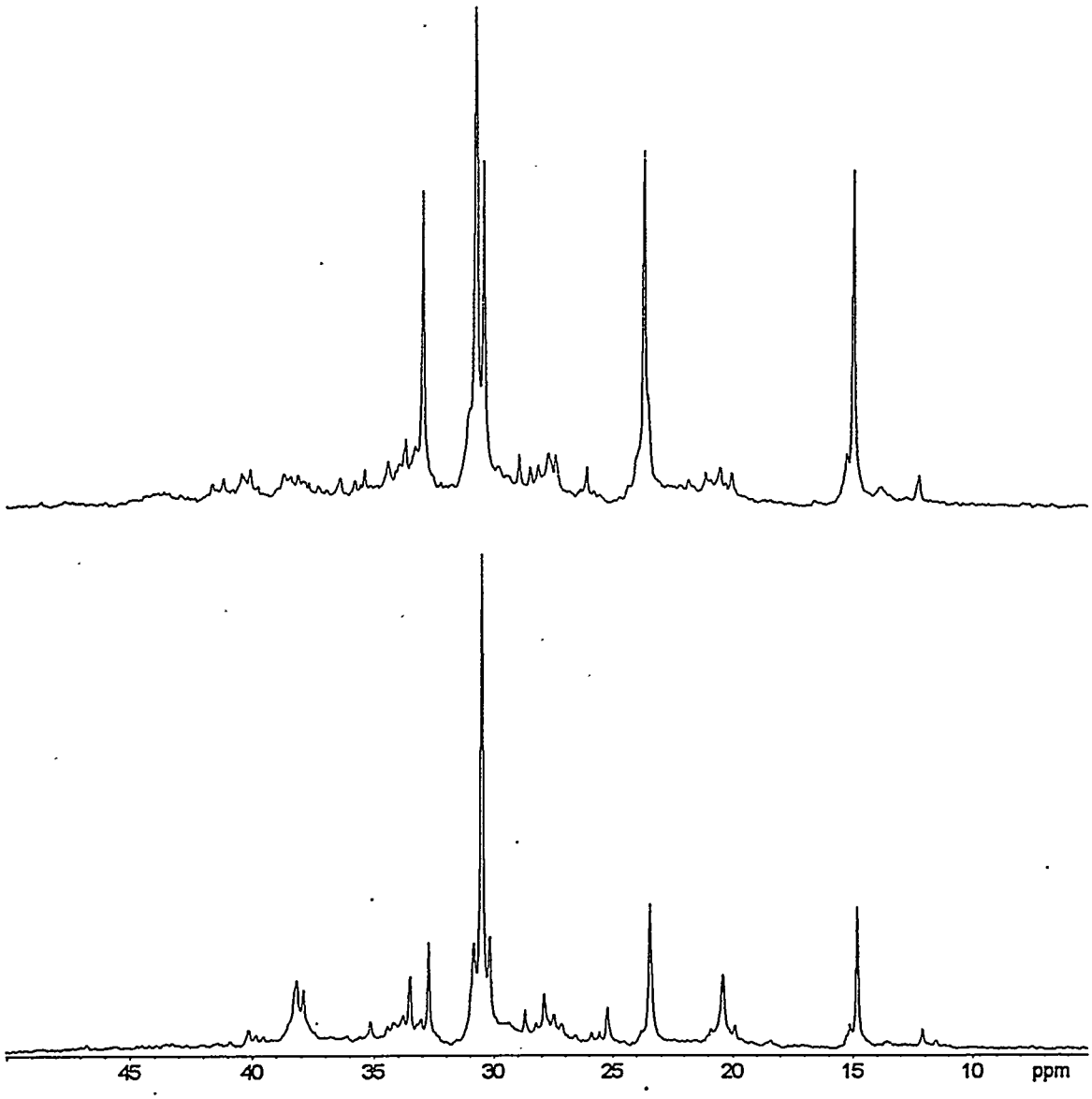
DURSC.DAT (85-140 PPM)



DURFC.DAT (85-140 PPM)

Fig. 4

DR1SC.DAT (5-50 PPM)



DR1FC.DAT (5-50 PPM)

Figure 5. Possible hydrocracking reactions of Drakeol 34

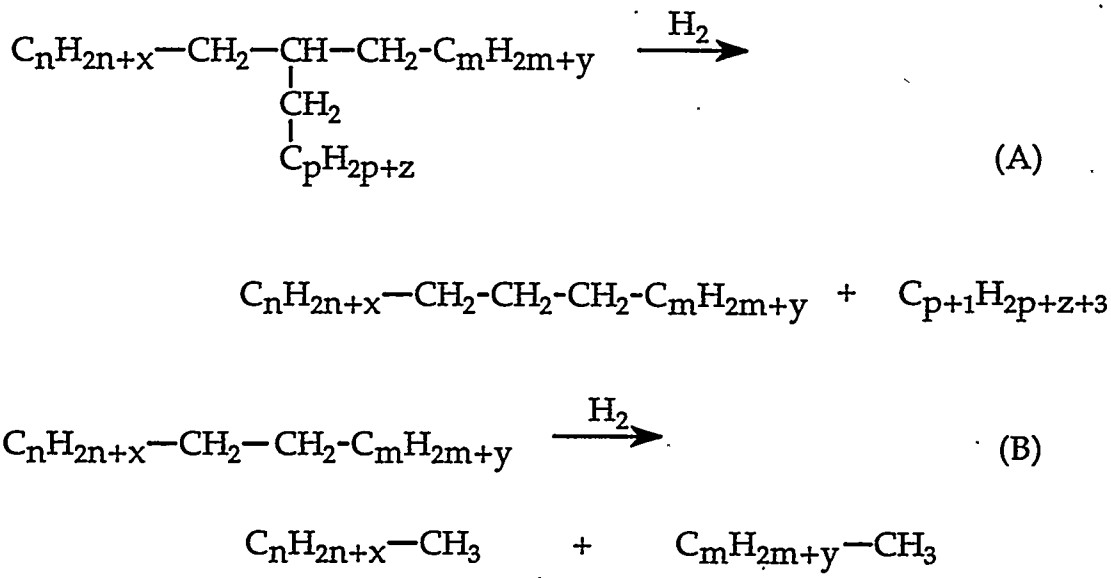
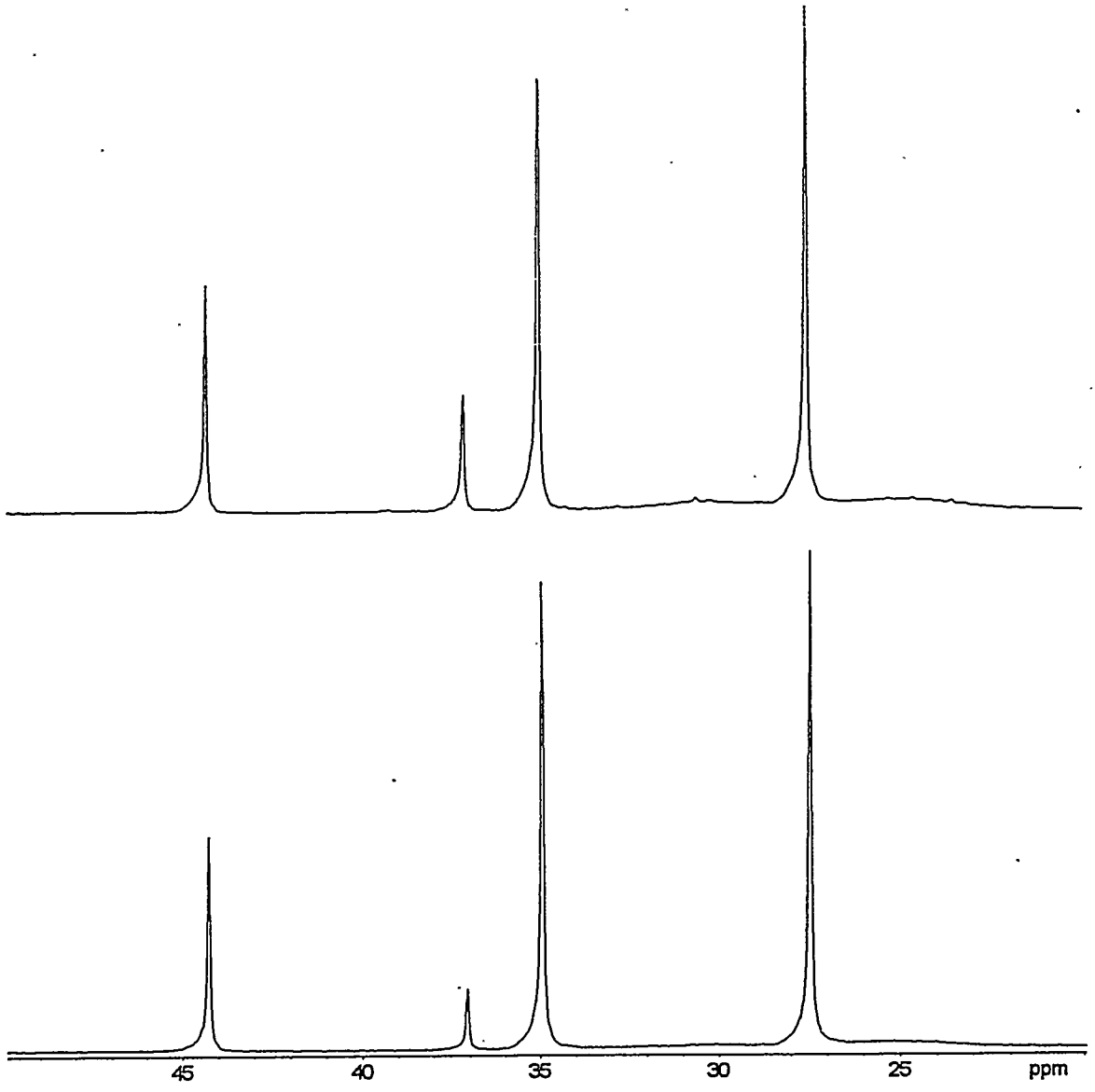


Fig. 6

DECSC.DAT (20-50 PPM)



DECFC.DAT (20-50 PPM)

Figure 7. Possible hydrocracking reactions of decahydronaphthalene

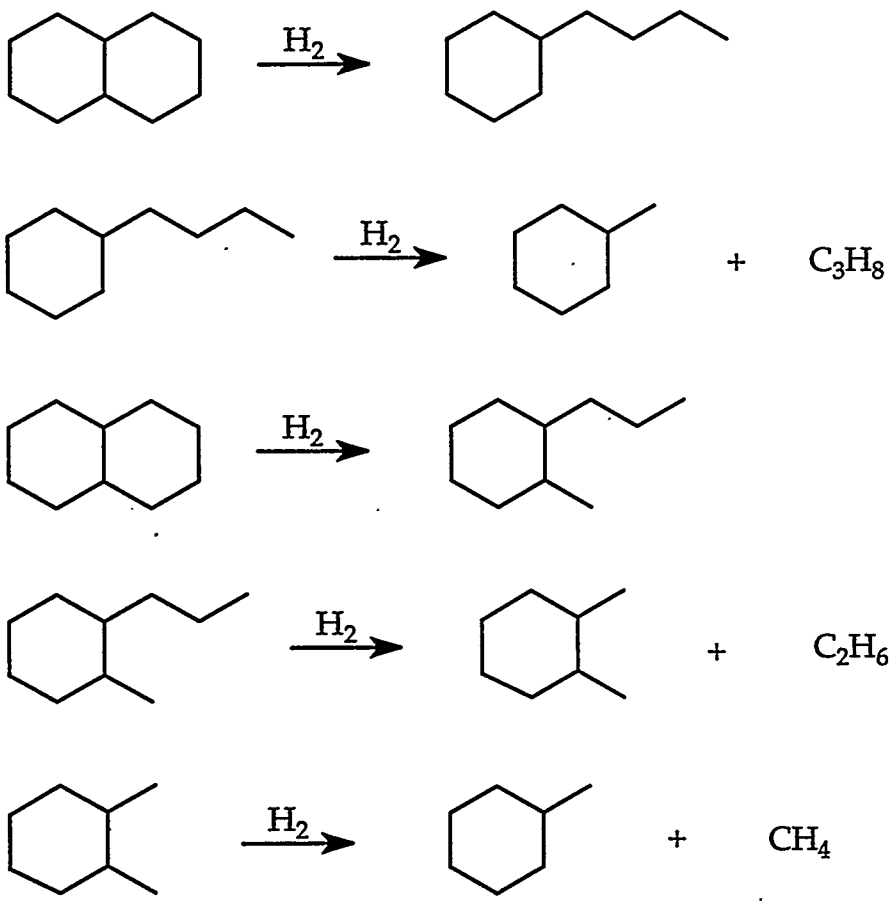
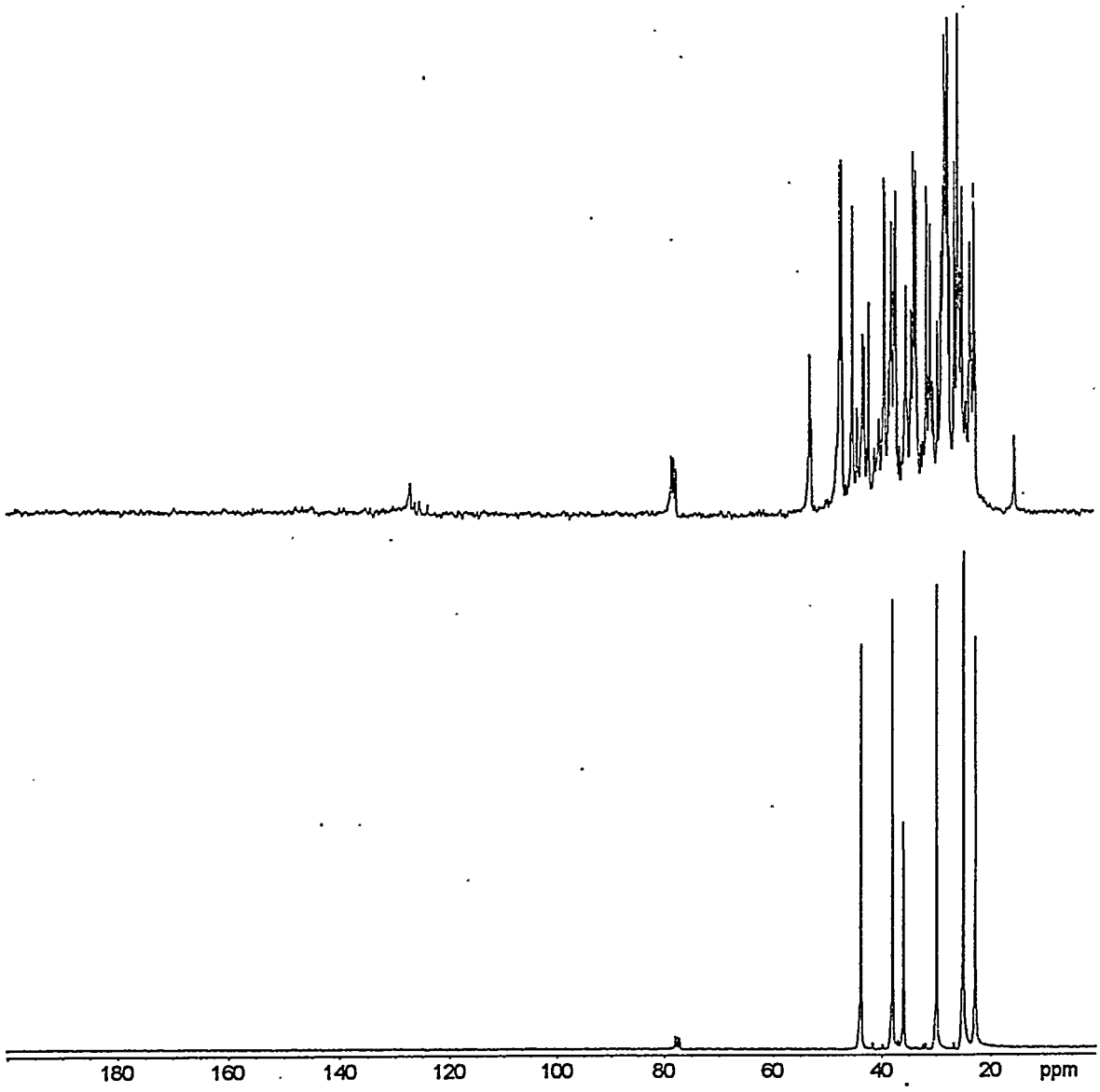


Fig. 8

PHFSC.DAT (0-200 PPM)



PHFFC.DAT (0-200 PPM)

Figure 9. Possible hydrocracking reactions of perhydrofluorene

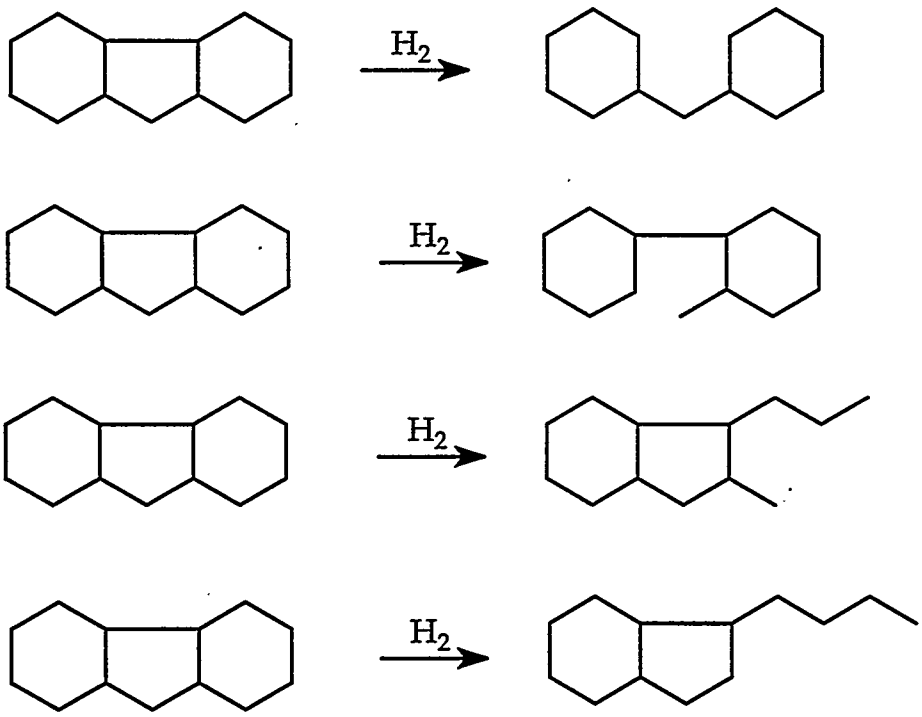
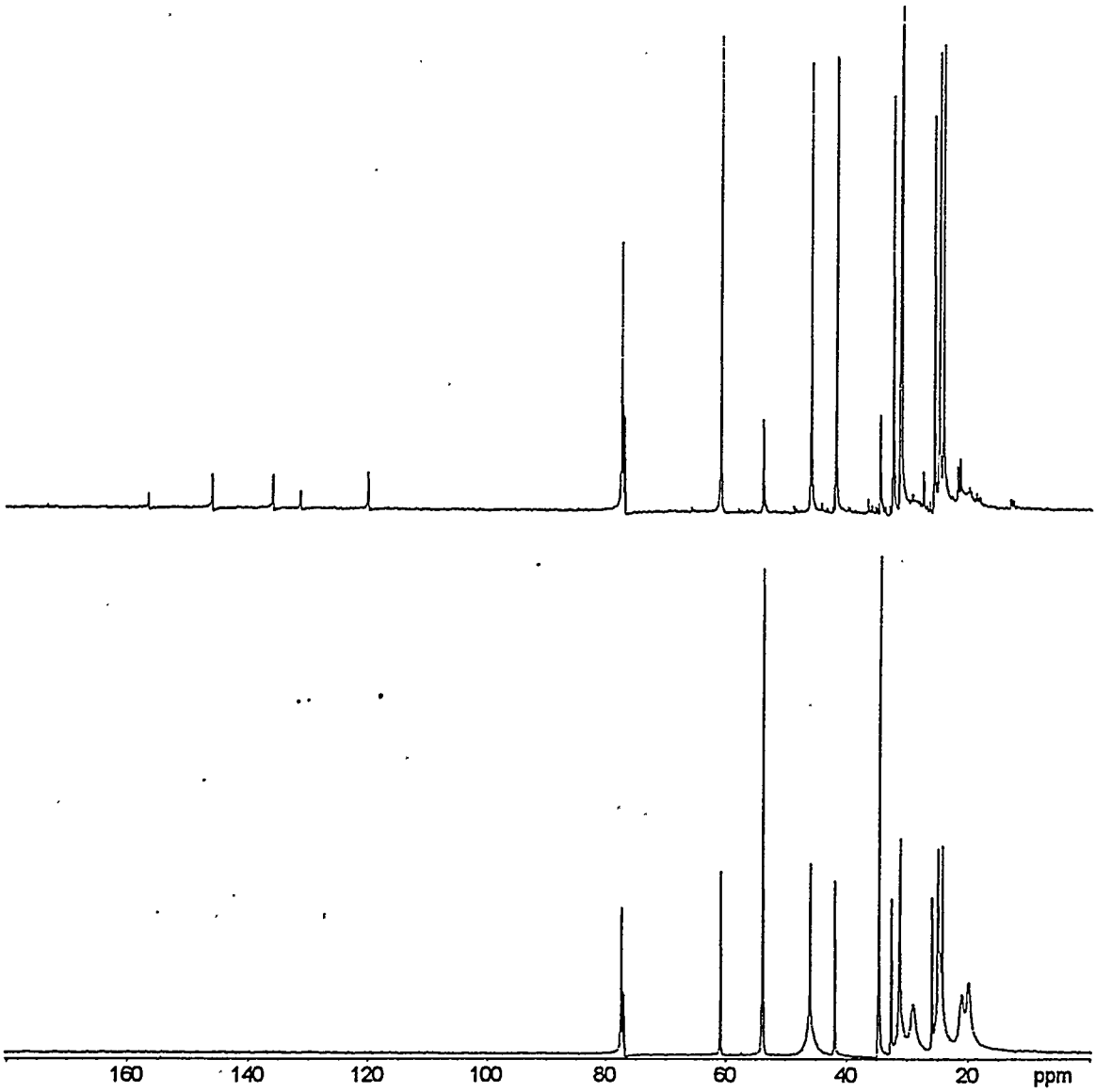


Fig. 10

DHQSPC.DAT (0-180 PPM)



DHQFRC.DAT (0-180 PPM)

Figure 11. Possible reactions in tetrahydronaphthalene decomposition at 425 °C

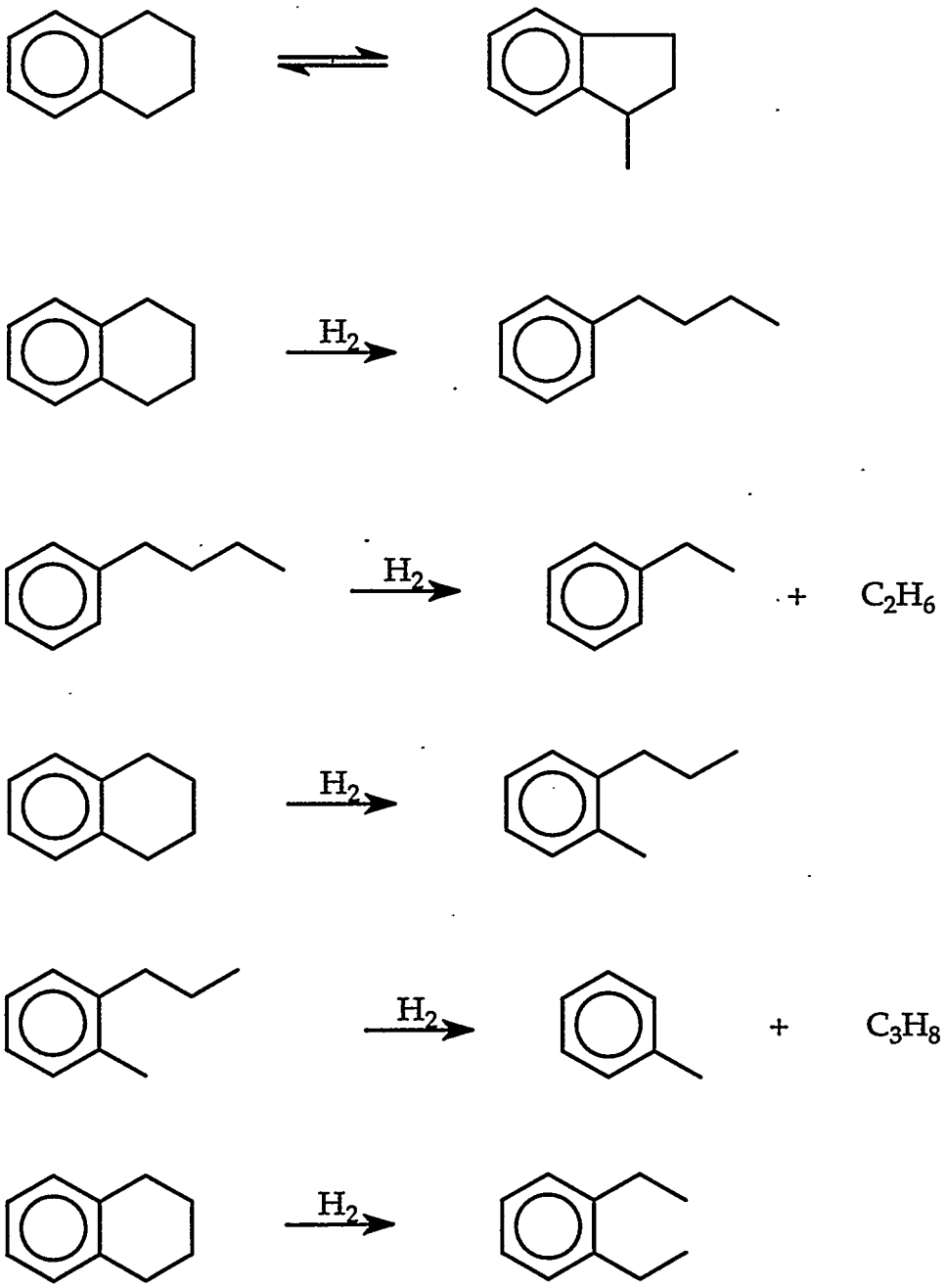


Figure 12. Possible reactions in tetrahydroquinoline decomposition at 375 °C

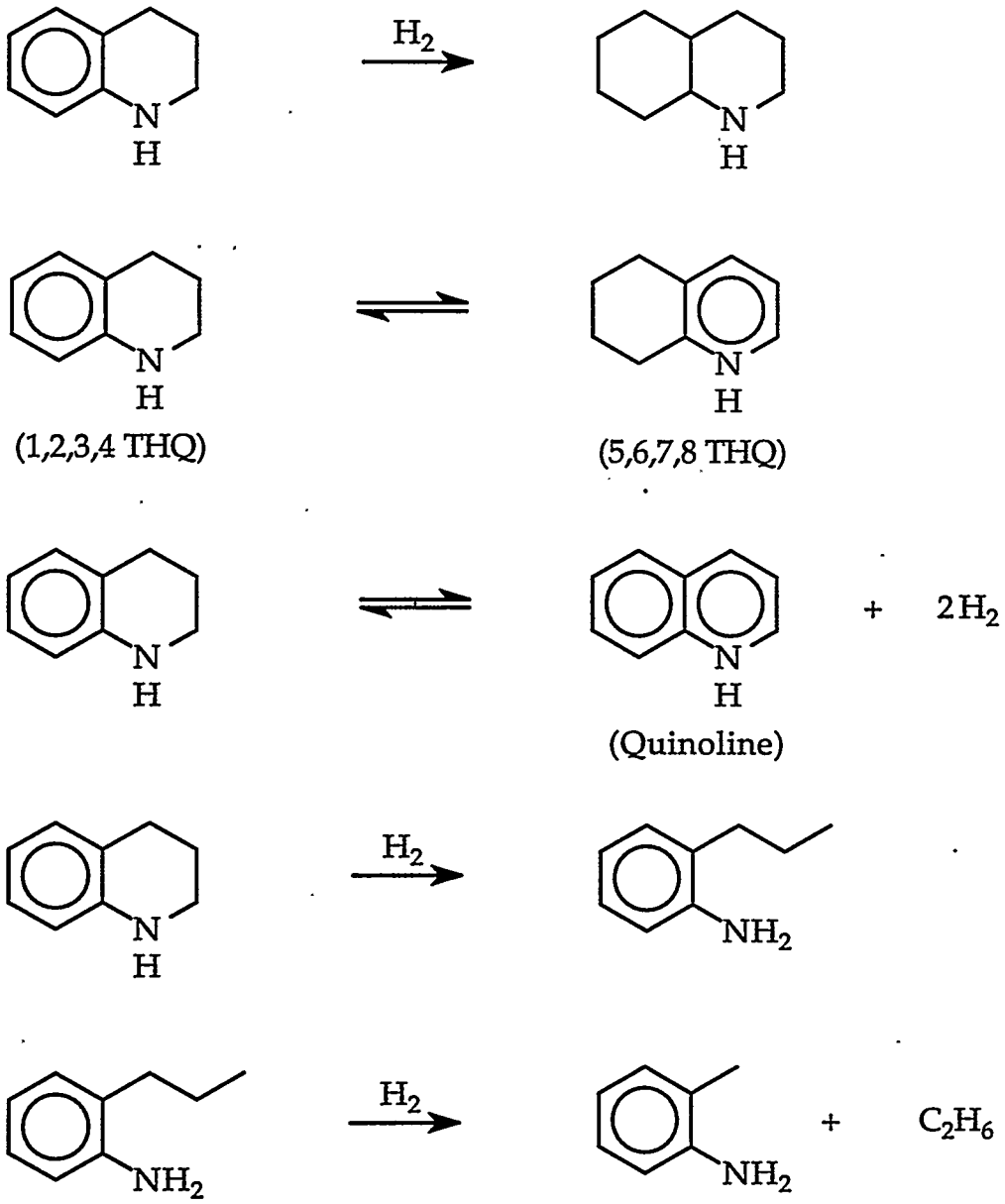
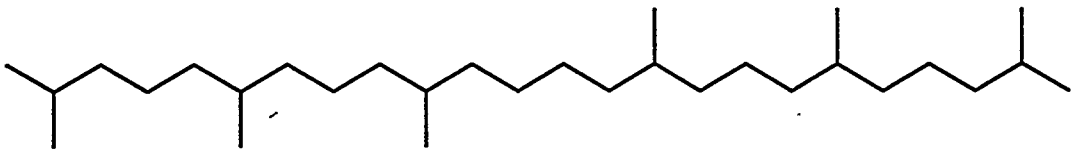
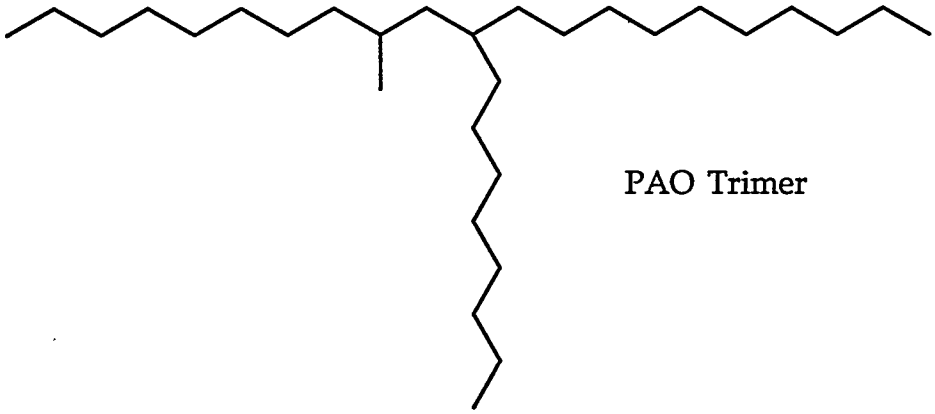


Figure 13.- Chemical Structures of Squalane and the Hydrogenated Trimer of 1-Decene



Squalane



PAO Trimer

Table 1

Liquid Characteristics

Liquid Designation	Composition (Formula)	Boiling Point (°C) [1,2]	Molecular Weight [2]	Specific Gravity @20°C [2]	Supplier/ Source
Durasyn 180	Hydrogenated homopolymer of 1-decene (100 % paraffinic)	385 @ IB	2000 (average)	0.845-0.855	Albemarle
Drakeol 34	Mineral oil (68% paraffinic 32% naphthenic)	437 @ IB 489 @ 50% 529 @ 90%	492 (average)	0.858-0.872	Penreco
DHN (Decalin)	Decahydro-naphthalene ($C_{10}H_{18}$)	cis: 195.8 trans: 187.3	138.25	cis: 0.896 trans: 0.870	DuPont
PHF	Perhydrofluorene ($C_{13}H_{22}$)	260	178.32	0.920	Aldrich
DHQ	Decahydro-quinoline ($C_9H_{17}N$)	cis: 206 trans: 204	139.24	cis: 0.943 trans: 0.961	Fischer
134PPDP	1,3-di-4-pyperidylpropane ($C_{13}H_{26}N_2$)	329	210.36	-	Reilly
NB37	Naphthenic Base 37 (100% naphthenic)	-	-	0.864	Lagoven
THN (tetralin)	Tetrahydro-naphthalene ($C_{10}H_{12}$)	207.6	132.21	0.966	Fischer
THQ	Tetrahydro-quinoline ($C_9H_{11}N$)	251	133.19	1.059	Fischer

[1] Data for Drakeol 34 obtained per ASTM D 1160 Distillation @ 760 mmHg; for Durasyn per experimental measurement (McCutchen, 1996). "IB" indicates the temperature at which boiling was first observed; "50%" and "90%" indicate the temperatures at which 50 and 90 vol % of the mixture had boiled off, respectively.

[2] Data sources are provided in Márquez (1996)

Table 2

Summary of Results of Thermal Stability Tests

Liquid	Initial weight of liquid charged to reactor (gr)	Rate of C_1-C_4 gas production (g/hr)		Rate of liquid loss as C_1-C_4 gases (% of initial charge/hr)		Total weight of C_1-C_4 gases produced (gr)	Liquid Lost as C_1-C_4 gases (wt %)	Total weight of liquid lost (%)
		Maximum	Steady-State	Maximum	Steady-State			
Durasyn 180	127.50	2.3	0.15	1.8	0.12	-	-	65.0
Drakeol 34	129.75	1.6	0.13	1.2	0.10	-	-	59.0
DHN	132.45	0.13	0.0053	0.095	0.0040	-	-	26.0
PHF	138.00	0.61	0.061	0.44	0.044	-	-	9.0
DHQ	100.44	0.17	0.066	0.17	0.066	5.2	5.2	31.0
134PPDP	101.50	0.22	0.0019	0.22	0.0020	1.7	1.7	30.0
NB37	100.00	0.42	0.13	0.42	0.12	16	16	40.8
THN	149.74	0.019	0.0036	0.012	0.0020	0.19	0.12	13.0
THN (@ 425°C)	155.37	0.063	0.024	0.041	0.015	2.6	1.7	10.0
THQ	160.10	0.16	0.013	0.10	0.0080	3.4	2.2	9.0

Table 3

Selected Properties of Durasyn 180

	Fresh Sample	Sample after TST
Molecular weight [1]	1449	198
Density, d (gr/cc) [2,3]	0.8495	0.7906
Refractive index, η [3]	1.4733	1.4429
Appearance	colorless, very viscous	yellow, non-viscous
% aromatics (% A) [4]	0.7	5.0
% naphthenics (% N) [4]	6.5	12.9
% paraffinics (% P) [4]	92.8	82.1

[1] Analysis by outside laboratory using vapor pressure osmometry (ASTM Test Method D2502-82).

[2] Analysis by outside laboratory using ASTM Test Method D1480-91.

[3] at 20°C

[4] calculated by the n-d-M method

Table 4

Selected Properties of Drakeol 34

	Fresh Sample	Sample after TST
Molecular weight [1]	405	264
Density, d (gr/cc) [2,3]	0.8656	0.8356
Refractive index, η [3]	1.4772	1.4612
Appearance	colorless and viscous	yellow and non-viscous
% aromatics (% A) [4]	3.0	1.0
% naphthenics (% N).[4]	31.7	39.0
% paraffinics (% P) [4]	65.3	60.0
Ra [4,5]	0.1	0.0
Rn [4,5]	1.9	1.3
Rt [4,5]	2.0	1.3

[1] Analysis by outside laboratory using vapor phase osmometry (ASTM Test Method D2502-82)

[2] Analysis by outside laboratory using ASTM Test Method D1480-91

[3] at 20°C

[4] calculated by the n-d-M method

[5] Ra, Rn, Rt are the average number of aromatic (a), naphthenic (n) and total (t) rings per molecule.

Table 5

Estimated Composition and Molecular Weight of Fresh Decahydronaphthalene Based on GC/MS Analysis

Sample: As-Received Decahydronaphthalene

Component	Retention time (min)	Probability (%)	Molecular Formula	Molecular Weight	mol %
Trans-decahydronaphthalene	9.88	98	$C_{10}H_{18}$	138	63.9
Cis-decahydronaphthalene	10.67	94	$C_{10}H_{18}$	138	36.1
Total					100
Average MW (gr/mol)				**138**	

Table 6

Estimated Composition and Molecular Weight of Spent Decahydronaphthalene Based on GC/MS Analysis

Sample: Decahydronaphthalene after Thermal Stability Test @ 375 °C for 72 hours

Component	Retention time (min)	Probability (%)	Molecular Formula	Molecular Weight	mol %
Trans-decahydronaphthalene	9.99	87	$C_{10}H_{18}$	138	61.1
Cis-decahydronaphthalene	10.77	86	$C_{10}H_{18}$	138	38.9
Total					100
Average MW (gr/mol)				**138**	

Table 7

Estimated Composition and Molecular Weight of Spent PHF Based on GC/MS Analysis[1]

Sample: Perhydrofluorene after Thermal Stability Test @ 375°C for 72 hours

Component	Retention time (min)	Probability (%)	Molecular Formula	Molecular Weight	mol %
cis-octahydro indene	8.48	97	C_9H_{16}	124	0.2
cis-decahydronaphthalene	8.80	48	$C_{10}H_{18}$	138	0.1
octahydro-5-methyl indene	9.42	99	$C_{10}H_{18}$	138	0.6
trans-5-methyl-3-(1-methylethenyl)-cyclohexene	9.68	90	$C_{10}H_{16}$	136	0.1
trans-8-methylbicyclo[4.3.0] non-3-ene	9.96	78	$C_{10}H_{16}$	136	0.2
2,3-dihydro-1-methyl indene	10.29	74	$C_{10}H_{12}$	132	0.1
MW 180	14.11	See footnote 2	$C_{13}H_{24}$	180	2.0
MW 180	14.62	See footnote 2	$C_{13}H_{24}$	180	2.9
MW 180	14.68	See footnote 2	$C_{13}H_{24}$	180	1.3
MW 178	14.76	See footnote 2	$C_{13}H_{22}$	178	4.5
MW 178	15.00	See footnote 2	$C_{13}H_{22}$	178	3.0
PHF	**15.27**	**66**	**$C_{13}H_{22}$**	**178**	**43.2**
MW 178 ?	15.45	See footnote 2	$C_{13}H_{22}$	178	3.8
PHF Isomer	15.70	88	$C_{13}H_{22}$	178	20.7
PHF Isomer	15.82	59	$C_{13}H_{22}$	178	13.2
PHF Isomer	16.23	See footnote 2	$C_{13}H_{22}$	178	4.0
Total					100
Average MW (gr/mol)				**178**	
% MW reduction				**0**	

[1] contribution of unknown components with BP > 300 °C assumed to be negligible

[2] no library spectra were found that matched the unknown

Table 8

Estimated Composition and Molecular Weight of Spent Decahydroquinoline Based on GC/MS Analysis[1]

Sample: Decahydroquinoline (DHQ) after Thermal Stability Test @ 375 °C for 72 hours

Component	Retention time (min)	Probability (% accuracy)	Molecular Formula	Molecular Weight	mol %
MW 138	9.61	30	$C_{10}H_{18}$	138	0.5
MW 138	10.44	47	$C_{10}H_{18}$	138	0.9
MW 141 [3]	10.75	See footnote 2	$C_9H_{19}N$	141	3.2
trans-DHQ	**11.33**	**73**	**$C_9H_{17}N$**	**139**	**83.3**
cis-DHQ	**11.93**	**32**	**$C_9H_{17}N$**	**139**	**11.1**
THQ	12.70	69	$C_9H_{11}N$	133	1.0
Total					100
Average MW (gr/mol)				**139**	
% MW reduction				**none**	

[1] contribution of unknown components with BP > 300 °C assumed to be negligible
[2] no library spectra were found that matched the unknown
[3] possibly butyl piperidene

Table 9

Estimated Composition and Molecular Weight of Spent 134 PPDP Based on GC/MS Analysis[1]

Sample: 1,3-Di-4-Piperidylpropane after Thermal Stability Test @ 375 °C for 72 hrs

Component	Retention time (min)	Probability (% accuracy)	Molecular Formula	Molecular Weight	mol %
ethyl cyclopentane	3.34	64	C_7H_{14}	98	3.4
methyl pyridine	5.29	97	C_6H_7N	93	10.2
nonane	5.81	83	C_9H_{20}	128	4.5
ethyl pyridine	7.07	94	C_7H_9N	107	11.2
trimethyl pyridine	8.17	62	$C_8H_{11}N$	121	1.7
dimethyl nonane	8.76	52	$C_{11}H_{24}$	156	11.9
trimethylpyridine	9.22	69	$C_8H_{11}N$	121	2.2
dimethyl hexane	11.35	45	$C_{13}H_{28}$	184	2.8
MW 182	12.79	See footnote 2		182	12.1
hexyl pyridine	13.72	60	$C_{11}H_{17}N$	163	7.8
MW 180	14.16	See footnote 2		180	12.7
heptyl pyridine (or isomer)	14.75	36	$C_{12}H_{19}N$	177	2.5
octyl pyridine	16.11	20	$C_{13}H_{21}N$	191	5.6
MW 205	16.65	See footnote 2		205	2.0
MW 189	17.52	See footnote 2	$C_{12}N_{19}N$	189	9.3
Total					100.0
Average MW (gr/mol)				**154**	
% MW reduction				**27**	

[1] contribution of unknown components with BP > 300 °C assumed to be negligible

[2] no library spectra were found which matched the unknown

Table 10

Properties of Naphthenic Base 37 (NB37)

API Gravity @ 15.5 °C (60 °F)	32.2
Specific Gravity @ 15.5 °C (60 °F)	0.8644
ASTM Color	0.5
Flash Point (°C)	178
Viscosity Index	84
Carbon Conradson (wt %)	0.01
Aniline Point (°C)	87.8
Kinematic viscosity @ 40 °C (104 °F) (cst)	13.89
Kinematic viscosity @ 100 °C (212 °F) (cst)	3.17

Table 11

Estimated Composition and Molecular Weight of Spent Tetralin Based on GC/MS Analysis[1]

Sample: Tetralin after Thermal Stability Test @ 375 °C for 72 hr

Component	Retention time (min)	Probability (% accuracy)	Molecular Formula	Molecular Weight	mol %
methyl dihydroindene	10.26	86	$C_{10}H_{12}$	132	3.8
Tetralin	**11.80**	**97**	**$C_{10}H_{12}$**	**132**	**96.2**
Total					100
Average MW (gr/mol)				**132**	
% MW reduction				**none**	

[1] contribution of unknown components with BP > 300 °C assumed to be negligible

Table 12

Estimated Composition and Molecular Weight of Spent Tetralin from a Thermal Stability Test at 425°C, Based on GC/MS Analysis[1]

Sample: Tetralin after Thermal Stability Test @ 425 °C for 72 hr

Component	Retention time (min)	Probability (% accuracy)	Molecular Formula	MW (gr/mol)	mol %
toluene	4.16	94	C_7H_8	92	1.4
ethylbenzene	5.94	94	C_8H_{10}	106	2.3
methyl propyl benzene	8.86	86	$C_{10}H_{14}$	134	0.8
butyl benzene	9.90	84	$C_{10}H_{14}$	134	17.5
methyl dihydroindene	10.40	75	$C_{10}H_{12}$	132	32.5
Tetrahydronaphthalene	**11.90**	**95**	**$C_{10}H_{12}$**	**132**	**42.2**
naphthalene	12.73	97	$C_{10}H_8$	128	3.3
Total					100
Average MW (gr/mol)				**131**	
% of MW reduction				**1**	

[1] contribution of unknown components with BP > 300 °C assumed to be negligible

Table 13

Estimated Composition and Molecular Weight of Spent THQ Based on GC/MS Analysis[1]

Sample: Tetrahydroquinoline after Thermal Stability Test @ 375 °C for 72 hr

Component	Retention time (min)	Probability (% accuracy)	Molecular Formula	Molecular Weight	mol %
methyl benzenamine	9.96	96	C_7H_9N	107	1.5
trans-decahydroquinoline	11.28	83	$C_9H_{17}N$	139	0.8
ethyl benzenamine	11.49	50	$C_8H_{11}N$	121	0.4
tetrahydronaphthalene	11.56	97	$C_{10}H_{12}$	132	0.5
MW 135	12.52	52	C_8H_9NO	135	0.9
5,6,7,8-THQ	12.64	71	$C_9H_{11}N$	133	9.0
quinoline	13.00	62	C_9H_7N	129	7.5
THQ (1,2,3,4)	**14.65**	**88**	**$C_9H_{11}N$**	**133**	**75.3**
MW 147	14.72	52	$C_{10}H_{13}N$	147	2.2
MW 147	15.12	46	$C_{10}H_{13}N$	147	0.1
MW 161	15.27	41	$C_{11}H_{15}N$	161	0.2
ethyl quinoline	15.35	71	$C_{11}H_{11}N$	157	0.9
MW 147	15.69	42	$C_{10}H_{13}N$	147	0.2
MW 161	16.23	See footnote 2		161	0.6
Total					100
Average MW (gr/mol)				**133**	
% MW reduction				**none**	

[1] contribution of unknown components with BP > 300 °C assumed to be negligible

[2] no library spectra were found which matched the unknown