# EFFECTS OF TITANOCENE DICHLORIDE ON FREE RADICAL FORMATION DURING TREATMENT OF A COAL-DERIVED LIQUID

By

WICHAI MAHORANKIT

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Chulalongkorn University

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Thesis Approved:

Mayis Seapan
Thesis Adviser

Robert L. Robinson, Jr.

M. M. Johnson

Norman N. Durham
Dean of the Graduate College

# ABSTRACT

Catalyst deactivation is a major problem in catalytic hydrotreatment of coal-derived liquids. Adding certain additives to feedstocks is one potential technique to retard catalyst deactivation and improve catalyst activity. Titanocene dichloride exhibited this characteristic to reduce coke formation and promote catalyst activities in hydrotreatment of a coal-derived liquid. The role of titanocene dichloride on the improvement was suspected to be due to the free radicals generated by the decomposition of titanocene dichloride.

The experiments with treating the undoctored and doctored feedstocks under various conditions were conducted in a trickle-bed reactor system. The effects of titanocene dichloride on the free radical formation during the process were studied by using Electron Spin Resonance spectroscopy. The effects of titanocene dichloride on catalyst activity were evaluated by determinations of elemental composition and boiling range ditribution of the treated oil. The effects of titanocene dichloride on catalyst deactivation were also studied by characterization of the aged catalyst.

The presence of titanocene dichloride in the feedstock increased the formation of free radicals in the entire temperature range of 250 C to 400 C, with rates of recombination and hydrogen capping reactions strongly affecting the concentration of free radicals in the products. The catalyst showed a significant effect on free radicals, catalyzing their reaction with hydrogen and reducing their concentration. Free radicals appear to be formed by two different mechanisms in the lower (about 250 C) and higher (about 375 C) temperature ranges. Titanocene dichloride appeared to slightly promote HDN at temperatures higher than 350 C. Although no coke suppression was observed with the presence of titanocene dichloride, the loss of catalyst pore volume and surface area was reduced with the doctored feeds. Several profiles of the titanium deposit within the spent catalysts were observed along the reactor under nitrogen atmosphere, whereas the titanium deposit within the catalysts from the hydrotreating runs had a shell-maximum profile. Coke formation on the spent catalysts under hydrogen and nitrogen atmospheres is caused by different coking mechanisms. Two distinctly different coking profiles along the reactor were observed under hydrogen and nitrogen atmospheres.

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# CHAPTER I

# INTRODUCTION

## INTRODUCTION

Coal-derived liquids contain undesirable elements of sulfur, nitrogen, oxygen and trace metals. Removing these contaminants from fuels is necessary for environmental and processing reasons. Therefore, it is essential for coal-derived liquids to be upgraded. The upgrading is usually accomplished by catalytic hydrotreatment.

In catalytic hydrotreatment, catalyst deactivation is a major problem. Many techniques have been proposed to prolong the catalyst life and conserve catalyst activities during operation. Adding titanocene dichloride in feedstocks was found to improve the catalytic hydrotreatment activities and reduce coke formation on the catalysts [Chan et al., 1982; Tscheikuna and Seapan, 1985]. The effects of titanocene dichloride were suspected to involve the organic free radicals generated from the interaction of titanocene dichloride with the components of oil during the process. A preliminary study on the effects of titanocene dichloride on the free radical formation in a coal-derived liquid was recently conducted by Wandke [1987].

The aim of this work is to investigate the effects of adding titanocene dichloride on the free radical formation in a coal-derived liquid during various treatments of a Solvent Refined Coal II (SRC-II) process solvent. Special attention is given to the effects of titanocene dichloride on catalyst activities and deactivation.

The main presentation of this study is given in Chapter II in a publication manuscript format. Since most experimental and analytical procedures in this study are employed and described by earlier investigators, only a brief discussion of experimental and analytical procedures are presented in Chapter II. Full detail of these procedures can be found in other theses [Bhan, 1983; Tscheikuna, 1985; Wandke, 1987]. The conclusions and recommendations of this thesis are given in Chapter III.

In addition, the experimental data of product analyses are given in the Appendices: Appendix A gives the results of Electron Spin Resonance measurements, Appendix B lists the elemental analysis data, and Appendix C shows the results of simulated distillation.

# CHAPTER II

# EFFECTS OF TITANOCENE DICHLORIDE ON FREE RADICAL FORMATION DURING TREATMENT OF A COAL-DERIVED LIQUID

# EFFECTS OF TITANOCENE DICHLORIDE ON FREE RADICAL FORMATION DURING TREATMENT OF A COAL-DERIVED LIQUID

Wichai Mahorankit

and

Mayis Seapan

School of Chemical Engineering
Oklahoma State University
Stillwater, OK 74078

# EFFECTS OF TITANOCENE DICHLORIDE ON FREE RADICAL FORMATION DURING TREATMENT OF A COAL-DERIVED LIQUID

## ABSTRACT

The effects of titanocene dichloride on the free radical formation during the treatment of an SRC-II process solvent under various conditions were studied by using Electron Spin Resonance (ESR) Spectroscopy. The experiments with treating the undoctored feedstock and the feedstock doctored with 100 ppm titanium as titanocene dichloride were conducted in a trickle-bed reactor system. The free radical formation was controlled by process conditions such as the presence of a catalyst, temperature, and the type of gaseous atmosphere. The free radical concentrations of the product oils were significantly affected by the presence of a Ni-Mo/alumina (Shell-324) catalyst. The highest radical concentrations were observed under the nitrogen atmosphere while the lowest were found under the hydrogen atmosphere. The presence of titanocene dichloride in the feed affected the free radical formation; however, this effect appeared to depend on process conditions. In the catalytic runs, two different coking tendencies along the reactor were observed under nitrogen and hydrogen atmospheres. Titanium deposit distributions within a catalyst pellet withdrawn from the catalytic hydrotreatment of the doctored feed runs were found to have

a shell maximum profile. Titanocene dichloride reduced the loss of the pore volume and surface area of the aged catalysts. Titanocene dichloride also slightly improved the hydrodenitrogenation activity of the catalyst.

## INTRODUCTION

Coal-derived liquids contain contaminants of sulfur, nitrogen, oxygen, and trace metals. Removing these contaminants from fuels is necessary for environmental and processing reasons. Therefore, it is essential for coal-derived liquids to be upgraded. The upgrading is usually accomplished by catalytic hydrotreatment. Ni-Mo/alumina and Co-Mo/alumina catalysts are commonly used in this process.

Several reactions including hydrogenation, hydrodesulfurization (HDS), hydrodeoxygenation (HDO), hydrodenitrogenation (HDN), and hydrodemetallation (HDM) occur during the catalytic hydrotreatment of coal-derived liquids. Green et al. [1985] attempted to relate the analyses of hydrotreated products of Solvent Refined Coal (SRC II) to the degrees of operating severity. They found that sulfur removal could be obtained under the mildest conditions, while oxygen and nitrogen removal required more severe conditions. The presence of high contents of nitrogen compounds in coal-liquids inhibited hydrodesulfurization [Sivasubramanian and Crynes, 1980;

Gutberlet and Bertolacini, 1983]. The rate of hydrodemetallation reaction appeared to be intraparticle diffusion controlled [Ammus et al., 1987].

Catalyst deactivation is a major concern in catalytic hydrotreatment of coal-derived liquids. The rates of catalyst deactivation in hydrotreatment of coal-derived liquids are higher than those of petroleum fuels due to the differences in feed composition [Stiegel et al., 1983]. The loss of catalyst activity during operation is caused by various mechanisms: the coverage of catalyst pores and active sites by carbonaceous deposits, known as catalyst coking; the poisoning of active sites and plugging of pores by metallic species; and the change in catalyst structure due to exposure to high temperatures, known as sintering. Sintering has a small effect in typical hydrotreatment [Stiegel et al., 1985]. Studies on deactivation of aged catalysts withdrawn from the hydrotreaters of two-stage coal liquefaction reactors from different plants showed similar results regarding the catalyst deactivation [Cable et al., 1985 (H-Coal Process); Stephens and Stohl, 1984 (Wilsonville); Stiegel et al., 1985 (Wilsonville)]. These results indicated that the loss of catalyst activity was initially rapid and primarily caused by coverage with carbonaceous cokes. The metal deposits gradually but permanently caused additional deactivation. The reduction of effective diffusivity of catalyst extrudates by both coke and metal deposits increased the deactivation effect. They also found that the rate of coking reached an equilibrium after a period of operation while the rate of metal deposition constantly decreased throughout the operation. Severe reduction in intraparticle diffusion due to coke and metal deposits was reported to contribute to catalyst deactivation in several studies [Prasher et al., 1978; Guin et al., 1986]. Stephens and Stohl [1984] described the different deactivation modes: uniform deactivation by carbonaceous cokes and shell progressive poisoning by metals.

Coke formation has been suspected to involve the adsorption on catalysts of precursors or deactivators contained in the feedstocks. The heavy fraction of coal-derived liquids was revealed to be a harmful fraction, causing serious catalyst deactivation [Stohl and Stephens, 1985; Yoshimura et al., 1987]. Cillo et al. [1985] suggested that pre-treatment such as deashing at low severity conditions of residua could decrease the deactivation rate of the harmful feeds. The observation of high C/H ratios, high contents of sulfur, oxygen, and nitrogen in the deposits on the catalysts indicated that polycyclic aromatics and hetero-polycyclic compounds contained in the feedstocks were among coke precusors [Furimsky, 1982; Stohl and Stephens, 1986; Ammus et al., 1987]. Coking tendencies were also reported to depend on different organic compounds [Scaroni and Jenkins, 1985; Stohl and Stephens, 1986]. The level of coke formation appeared to depend on the catalyst type and pore size [Chang and Crynes, 1986; and Ammus et al., 1987]. Lewis acidic sites on the hydrodesulfurization catalyst were observed to participate in coke formation reactions [Scaroni et al., 1984]. Klingman and Lee [1986] proposed a kinetic model to describe coke formation as multilayer deposition.

Although trace metal deposition does not show as a rapid deactivation effect as coke, its effect becomes more serious as a function of the operation period. Thus, the life-time of the catalyst is partially determined by trace metal deposition. Several major metals including titanium, iron, and calcium were found on aged catalysts. This observation indicated that these metals were the major contaminants in coal-derived liquids [Stiegel et al., 1985]. In the study of changes in metal contents in the feed before and after hydrocracking, Cloke et al. [1987] found that high contents of titanium and manganese were eliminated from the feed and deposited on the catalyst. No significant loss in the catalyst activity due to these metal deposits was observed in their study, except the loss of the ability to produce light fractions. J. Wei and R.G. Wei [1982] presented a mathematical model derived from a consecutive reaction path involving an intermediate reaction to describe several metal deposition patterns within a catalyst under different conditions of HDM. Despite the extensive studies of metal deposition on catalysts, the nature of the metallic species in coal-liquids and their generation mechanism during the liquefaction process are still unknown. Oxide states of several metals were found to cause catalyst deactivation; however, titanium in the form of an organometallic compound rather than the oxide form showed high affinity to be absorbed on the catalyst [Kovach et al., 1978]. In another study, the soluble organic titanium content in coal-derived liquids was found to be less than the detectability limits of the analytical technique [Robbat et al., 1984]. This observation suggested that titanium in coal-liquids probably did not exist in the organic form. As a result, the deposition of inorganic titanium in microparticulate or colloidal form was more likely to involve the catalyst deactivation. Robison and Filby [1985] studied the deposition of microparticles of titanium dioxide on the catalyst and observed only a little penetration of these crystals within the catalyst pores despite the abundance of smaller size crystals. Lynch [1985] studied the effect of titanium deposition on the catalyst deactivation by aging the catalyst with creosote oil doctored with titanium porphyrin. Although the regenerated spent catalyst of the doctored feed showed much higher titanium contents than those of undoctored feed, the catalyst activity in HDS and HDO of model compounds was slightly reduced. In fact, HDN activity appeared to be slightly improved.

Any attempt to suppress the deactivation and enhance the performance of the hydrotreating catalyst is valuable for the coal-derived liquid upgrading development. Adding certain additives in feedstocks has been one of the alternative techniques to improve the catalysts. Kukes et al. [1986] reported a better vanadium removal rate during hydroprocessing of the Maya feedstock doctored with 750 ppm phosphorus as triethyl phosphate over alundum and alumina. They proposed that phosphorus reacted with the feed homogeneously due to the observation of the initial activity resulting in the interstitial deposition of a vanadium-phosphorus species which promotes the activity of the heterogeneous reaction.

In our earilier investigation, adding titanocene dichloride to an SRC light oil improved the catalytic hydrotreatment activity of HDS, HDN, and HDO reactions and also reduced the coke formation on the catalyst [Chan et al., 1982]. This improvement depended on the titanocene dichloride concentrations added into the feed. Titanium concentrations of 100 ppm to 200 ppm showed the highest promotion of the catalyst activity. In a subsequent study, the effect of adding titanocene dichloride on the hydrogenation of different model hydrocarbons was evaluated. Experiments using tetralin as a low coking feedstock and a mixture of phenanthrene-tetralin as a high coking feedstock indicated that the effect of titanocene dichloride on the coke formation and hydrogenation activity depended on the type of hydrocarbon [Tscheikuna and Seapan, 1985]. The observed effects of titanocene dichloride were proposed to be due to the organic free radicals generated from the interaction of titanocene dichloride with organic molecules of oil during the process. Recently, a preliminary study of the effect of titanocene dichloride on the free radicals generated during the treatment of an SRC-II middle distillate under various conditions was conducted where the effects of titanocene dichloride on free radical formation were investigated by Electron Spin Resonance (ESR) spectrometry [Wandke, 1987]. By monitoring the changes in the free radical formation, potentially valuable information about the hydrotreating of coal-derived liquids may be obtained. Adding titanocene dichloride was also reported to promote the ability of the catalyst to produce low boiling fractions.

Electron Spin Resonance (ESR) spectroscopy is an excellent technique to study the free radicals in coals and their derived products [Petrakis and Grandy, 1978; 1979; Retcofsky et al., 1982; Yokono et al., 1983; Yamada et al., 1984]. The ESR measurement of free radicals is usually presented in terms of free radical concentrations and g-values. The reactions during thermal processing and hydroprocessing of coal and coal-derived products are generally thought to involve free radicals. The possible free radical reactions can be presented universally as: a) the thermal cleavage step resulting in free radical fragments, b) the stabilization step via a hydrogen donor system, c) the recombination and polymerization of radical fragments. Many studies of free radicals during coal pyrolysis and liquefaction have been done by using ESR [Petrakis and Grandy, 1980; 1981a; 1981b; Sprecher and Retcofsky, 1982; Rudnick and Tueting, 1984; Stenberg et al., 1985; Yokono et al., 1986]. In these studies, radical concentrations were usually found to increase with temperature; however, several different dependencies were also observed among various types of coals. These observations implied that the apparent increase in free radical concentration was the result of the total rate of decomposition and termination of the particular coal at the observed temperature. The presence of a good H-donor system resulted in a decrease in radical concentrations due to its effective ability in stabilizing radicals. The measured g-values of coal and coal-derived products showed the characteristics of aromatic hydrocarbons. Recently, Rudnick and Gudath [1986] studied the changes in radical concentrations during petroleum resid upgrading involving thermal and catalytic reactions by using ESR.

The purpose of this work is to investigate the effects of adding titanocene dichloride on free radical formation in a coal-derived liquid during various treatments of an SRC II process solvent. The experiments with treating the undoctored oil and the oil doctored with 100 ppm of Ti as titanocene dichloride feedstream were conducted in a trickle-bed reactor system. The experiments were performed in the temperature range of 250 C to 400 C under various processing conditions including catalytic, non-catalytic, and a nitrogen or hydrogen atmosphere. The changes of the free radicals in the products were monitored by the ESR measurement of the treated products and expressed in terms of product to feed radical concentration ratios and g-values. The effect of titanocene dichloride on catalyst deactivation was monitored on the coke formation, titanium distribution, and reduction of pore volume and surface area on the aged catalyst. The effects on the catalyst hydrotreatment activity were evaluated by determination of elemental composition and boiling range distribution of the treated oil.

## EXPERIMENTAL SECTION

### Materials

The coal-derived liquid feedstock used in this study was an SRC II process solvent (V-1074), obtained from Wilsonville coal liquefaction plant. The catalyst was a commercial Ni-Mo/alumina catalyst (Shell-324). Titanocene dichloride as the additive was a red crystalline solid compound supplied by Alpha Products. The analyses of the feedstock are given in Table I and those of the catalyst in Table II.

Procedure

All the experiments with treating the undoctored or doctored feed were conducted in a trickle-bed reactor system. This reactor system has been employed by several earlier investigators. A full discussion of the apparatus and experimental procedures is available elsewhere [Bhan, 1983; Tscheikuna, 1985]. The schematic diagram of the system is shown in Figure 1. The reactor system consists of two reactors in series equipped with an interstage sampling device. A set of sample bombs are connected to the second stage reactor. The product oil accumulated in these sample bombs can be taken periodically without disturbing the system operation. In this study, the second reactor was left empty; only the first reactor was employed.

All the experiments were conducted at a pressure of 10.4 MPa, a gas to oil ratio of 800 standard $m^3$ $H_2$ (or $N_2$)/$m^3$ oil, while the oil feed rate was maintained at 30 $cm^3/h$. The operating temperature was changed in 25 C increments from 250 C to 400 C and 300 C to 375 C with a period of 1 and 2 h for temperature stabilization at each desired temperature in the non-catalytic and catalytic runs respectively. The reactor was entirely packed with stainless steel cut-tubing pieces (1/8 inch O.D. 316 stainless steel tube cut to about 1/4 inch lengths) to provide good mixing and heating characteristic in the non-catalytic runs. In the catalytic runs, 10 grams of the catalyst was packed to about a 6 inch-high bed in the middle section of the reactor, while the upper and lower sections were filled with those stainless steel pieces. Before being used, this catalyst bed was calcined at 300 C for 1 h in $N_2$ at a pressure of 1730 kPa and a flow rate of 400 $cm^3$ STP/min. The reactor was then allowed to cool down to 250 C. The presulfudation was carried out from 250 C to 360 C at a rate of 5 C/min and maintained at 360 C for 2 h in a mixture of 5 vol % $H_2S$ in $H_2$ at a pressure of 555 kPa and a flow rate of 400 $cm^3$ STP/min. To reach the steady state in the catalytic runs, the system was operated at 300 C for 36 h. Samples were collected after 12, 24, 32 and 36 h during this period. The temperature-dependent samples were collected from 30-minute sample accummulations after each temperature stabilization period. A portion of each sample was taken in the ESR quartz tube and kept frozen in liquid nitrogen in order to trap the free radicals in the sample. The study of free radicals in oil samples stabilized in cryogenic liquid or a solidified matrix has been proposed to provide more information than studying free radicals without freezing them because of the short life of some reactive radicals [Rudnick and Tueting, 1984]. These ESR samples were then transported to the ESR Laboratory located in the Physics Department of Oklahoma State University for ESR measurements. The descriptions of the process conditions in each experimental run are summarized in Table III.

Twelve experiments were conducted in this study; however, the results from only ten runs were evaluated. The first run was a test run to evaluate the operation of the reactor. The other erroneous run was aborted due to an error in added titanium content. Each run was named to include the consecutive run number and three letters to indicate different process conditions. The first letter is designated for the type of gaseous atmosphere: N for nitrogen and H for hydrogen. The second letter is designated for the packing material: N for the non-catalytic and C for the catalytic condition. The last letter is designated for the feedstock: U for the undoctored feedstock and D for the doctored feedstock.

### Product Characterization

All the product samples were analyzed for carbon, hydrogen, nitrogen, titanium and iron contents. A Perkin Elmer Elemental Analyzer Model 240B was used for carbon, hydrogen and nitrogen analysis. The titanium and iron contents were determined by a Perkin Elmer 403 Atomic

Absorption Spectrometer. The oil samples were also analyzed for boiling range distribution by a simulated distillation method similar to the ASTM D-2887 technique with a Hewlett Packard Model 5880A Gas Chromatograph. The operating oven condition was set from the initial temperature of 40 C to the final temperature of 320 C with the heating rate of 7 C per minute. The correlation of the retention time and boiling temperature was calibrated by a mixture of normal paraffins, including $C_6$ to $C_{16}$.

## Catalyst Characterization

After each experiment, the catalyst section of the reactor was cut and separated into three parts marked as top, middle and bottom sections. The aged catalysts from each section were extracted with tetrahydrofuran in a Soxhlet apparatus for at least 24 h. The extracted samples were then analyzed for coke content, titanium distribution, pore volume and surface area. The coke content, defined as the THF insoluble carbonaceous material, was determined by the weight loss after oven combustion at 550 C in air for at least 72 h. A JEOL Model JFM-35 Scanning Electron Microscope equipped with an Energy Dispersive X-ray Analyzer (EDAX) was used for determination of titanium distribution in the aged catalysts. The pore volume and surface area of the aged catalysts were analyzed by an Autoscan 60 Porosimeter and the results were plotted by a Series 200 Omnigraph X-Y recorder.

## ESR Measurement

The ESR system consisted of a Brucker ER200D-SRC console, ER082 field modulator, BE-25 electromagnet, and IBM ER044 MRDH microwave bridge. All spectra were recorded at room temperature. The preliminary analysis showed that an absorption spectrum occurred at approximately 3325 gauss with frequency of about 9.28 GHz. All the analyses were therefore conducted with the center line at 3325 gauss with a scan range of 130 gauss. The other measurement conditions were set consistently throughout the analyses. Microwave power of 200 uW was employed in all the experiments. At sufficiently low microwave powers, where the ESR signal is proportional to the square root of the microwave power level, the spin concentration is proportional to the area of the double integration of the first derivative of the ESR spectrum where the other parameters are constant. Some experiments with microwave power variations showed that the measurement with power of 200 uW still provided the linear variation of the signal with the microwave field strength. The technique of measuring free radical concentration at various microwave powers has been employed to investigate the saturation behaviors of several coal macerals by Silbernagel et al. [1986]. Thus, the free radical concentration of each spectrum could be expressed as the area of the double integration of the first derivative spectrum. The area of each spectrum was calculated by a computer program developed at the Physics Department using a Hewlett Packard personal computer.

## RESULTS AND DISCUSSIONS

### Effects of Titanocene Dichloride on Free Radical Formation

Several ESR absorption spectra of the unfrozen feed were recorded at room temperature during a period of several months. All the results of these measurements showed almost identical spectra giving about the same area of the double integration and g-values of about 2.0028. This indicated that the observed radicals were the native radicals contained in the feed and were very stable. As a result, the presentation in terms of sample/feed free radical concentration ratio (gamma) is quite reasonable for observing the changes of radical concentrations in the treated products due to the constant free radical concentration in the feed. The comparisons of the gamma as a function of the operating temperature under the various process conditions of the undoctored and doctored products are shown in Figures 2 through 5.

For non-catalytic runs under a nitrogen atmosphere (Figure 2), the undoctored samples contained free radical concentrations corresponding to values of gamma ranging from 1.21 to 3.86. The concentration of free radicals remained essentially unchanged with temperature until about

350 C, above which it began to increase with temperature until 400 C, the maximum temperature studied. The results of two duplicate runs (2NNU and 6NNU) demonstrated quite good reproducibilty as shown in Figure 2. The doctored samples (12NND) had higher gamma values of 5.10 to 11.2, corresponding to about 3 to 4 times higher concentrations than those of the undoctored samples. The variation of gamma with temperature was more pronounced in the doctored samples. Basically, the free radical formation under the nitrogen/non-catalytic condition is likely due to the total rate of thermal decomposition and recombination of radical fragments. The presence of titanocene dichloride appeared to increase free radical concentrations under the nitrogen/non-catalytic condition, indicating that titanocene dichloride enhances free radical formation. Distinct increases of free radical concentration due to the presence of titanocene dichloride are probably generated not only by the cleavage of titanocene dichloride but also by the interaction of titanocene dichloride or its free radicals with components of the oil, resulting in more free radicals. Thus titanocene dichloride acts as a free radical initiator in this system.

In Run 2NNU and Run 12NND, the interstage samples were also collected. The results revealed the difference between the gamma values of the interstage samples and bottom samples. The differences were quite distintive for the interstage and bottom samples of Run 12NND (shown in Figure 2). This suggests that some free radicals in the oil were quite reactive and had very short life-times. They kept on reacting during the period of sample accumulation in the bottom sample bomb (about 30 min). Thus the time the free radicals remain untrapped (before being frozen in liquid nitrogen) should be kept as short as possible to obtain full information on the free radical behavior. Collection of interstage samples at high temperatures is difficult due to the evaporation effects in the interstage sampler and the resulting inconsistencies in the collection time. Because of this difficulty, the interstage samples were collected only in Runs 2NNU, 11HND and 12NND.

Figure 2 also shows that free radicals are produced by two different mechanisms. At lower temperatures of 250 C to 275 C, the free radicals are generated by a slow thermal mechanism. As a result the bottom samples, which have stayed at temperatures of about 200 C for a longer period than the interstage samples, show higher free radical concentrations. This phenomenon is observed for both the doctored (12NND) and the undoctored (2NNU) runs, except that the formation of free radicals is catalyzed by titanocene dichloride. As the temperature is increased, the rate of recombination of these radicals also increases such that a balance is established between the rates of generation and recombination of free radicals. Thus at temperatures around 300 C to 325 C, the free radical concentrations of the bottom and interstage samples approach each other. At temperatures higher than 350 C, a different mechanism causes the generation of free radicals. In this range the rate of generation of free radicals is higher than the rate of recombination and the rate of generation is catalyzed by titanocene dichloride or its by-products. It should be emphasized that titanocene dichloride catalyzes the free radical formation in the entire range of 250 C to 400 C.

The undoctored samples treated under the hydrogen/non-catalytic condition from Run 3HNU contained free radicals ranging from gamma values of 1.93 to 3.20. The variation of the free radical concentration in Run 3HNU with temperatures (shown in Figure 3) was quite small with temperature throughout the range of study. Although the results of Run 3HNU appeared to be similar to those of Run 2NNU and Run 6NNU in the temperature range of 250 C to 350 C, no increase of the gamma with temperature was observed in the temperature range of 350 C to 400 C. This indicates the role of radical stabilization under hydrogen pressure which essentially caps all the free radicals formed in this temperature range.

The doctored samples treated under the hydrogen/non-catalytic condition (Run 11HND) contained free radical concentrations higher than those of the undoctored samples, corresponding to the gamma values from 2.24 to 8.42 as shown in Figure 3. Titanocene dichloride clearly affected the free radical formation under the hydrogen/non-catalytic condition. Again the two different mechanisms of free radical formation are distinctly observable. At 250 C to 275 C, the bottom samples contain more free radicals than the interstage samples showing the slow mechanism of free radical formation. The catalytic effect of titanocene dichloride on the formation of free radicals is obvious in the bottom products in the range of 250 C to 350 C. However, at higher temperatures of 375 C and 400 C, the gamma of the bottom samples from the doctored run (11HND) decreases to about the same level as the undoctored samples. This indicates the effect of radical stabilization by hydrogen which dominates the rate of formation of free radicals and masks the effect of titanocene dichloride at temperatures above 350 C. However, the effect of titanocene dichloride is strongly noticeable for the interstage samples of Run 11HND, as a sharp increase of the gamma between the temperature range of 350 C to 400 C, as shown in Figure 3. This was just opposite to the observation of the lowest gamma in the bottom sample. The free radicals generated at these high temperatures resulting in high concentrations, have higher reactivity than low temperature radicals. Thus they recombine with each other or are stabilized by the molecular hydrogen. Therefore, the high free radical concentration in the interstage sample is rapidly reduced during the sample accummulation period in the bottom sample.

A sharp increase of free radical concentration in the interstage samples in the temperature range of 300 C to 350 C was also observed in the earlier study by Wandke [1987]. He found that this increase occurred in the presence of titanocene dichloride, regardless of processing conditions. He also found that free radical concentration decreased at temperatures higher than 350 C due to the domination of free radical termination reactions.

Figure 4 shows the presence of Shell 324 catalyst under $N_2$ pressure appeared to significantly increase the free radical formation, corresponding to high gamma values ranging from 15.0 to 21.4 for the undoctored samples and from 18.2 to 28.5 for the doctored samples. Sakawa et al. [1983] reported observing an increase in free radical concentrations during coal carbonization of some coal model compounds, such as naphthalene and anthracene with the presence of aluminium chloride as the catalyst. They proposed that the increase in free radical concentrations of the aromatic compounds having high frontier electron densities with aluminium chloride was probably due to the electrophilic reactions of aluminium chloride with those aromatic compounds. The effect of $ZnCl_2$ as the catalyst during coal liquefaction on the increase in radical concentration was also reported recently [Yokono et al., 1986].

The significant increase in the free radical concentration under catalytic conditions was likely due to, besides the thermal decomposition, the reactions of the active sites of the catalyst with the feed resulting in the cleavage of chemical bonds and formation of free radicals. The temperature dependencies of free radical concentrations appear to be different for undoctored (7NCU) and doctored (9NCD) samples as shown in Figure 4. The undoctored samples have relatively lower free radical concentrations at about 300 C, but the concentrations increase with temperature. The doctored samples, however, have a high free radical concentration at 300 C which shows a trend of decreasing free radical concentrations as a function of temperature in the range from 300 C to 375 C. Again the presence of titanocene dichloride in the feed catalyzed the free radical formation reactions, but as the temperature increased, the rate of recombination of free radicals also increased, reducing the concentration of free radicals.

Figure 5 shows that the free radical concentrations in the undoctored (5HCU and 8HCU) and doctored (10HCD) catalytically hydrogenated samples were quite lower than those treated under the other conditions, corresponding to gamma values ranging from 0.40 to 1.12 for the undoctored samples and 0.46 to 2.03 for the doctored samples. The observed gamma values were mostly lower than unity indicating that the free radical concentrations of samples were often lower than the original concentration in the feed. This indicates that the catalyst can significantly enhance the free radical stabilization reactions by the molecular hydrogen. Figure 5 shows that different free radical concentration dependencies upon temperature were found in the undoctored and doctored samples. The free radical concentrations of the undoctored samples (5HCU and 8HCU) decreased slowly from 300 C to 350 C, whereas the free radical concentration dropped rapidly in the range of 300 C to 325 C for the doctored samples (10HCD). This observation confirmed the effect of titanocene dichloride on the formation of free radicals under catalytic conditions also. When comparing the results under catalytic reactions under both nitrogen and hydrogen atmospheres, we noticed that the free radical concentration dependencies upon temperature were quite in the same pattern in both cases for either the undoctored or doctored samples, except that the concentrations presented under $H_2$ pressure had much lower values than those under the nitrogen atmosphere. This suggests that the presence of titanocene dichloride in the feedstock systematically affects free radical formation in catalytic reactions.

The measured g-value of the feed was 2.0028. The g-values of SRC process solvents and middle distillate have been reported to be about this value [Petrakis and Grandy, 1979; Yamada et al., 1984]. The measured g-values of all the treated samples varied slightly in a range of 2.0024 to 2.0027. The decrease of g-values of the treated sample under various conditions was probably due to the reduction in the heteroatom contents of the sample. No effect of titanocene dichloride on the change of the g-value could be noticed.

The g-value is particularly sensitive to the chemical environment of the unpaired electron in a free radical; in other words, it provides the information about the structure of a radical [Petrakis and Grandy, 1978]. Therefore, small changes in the observed g-values indicated that possible changes in the radical structure due to the loss of heteroatoms might happen during the reactions under various conditions.

### Effects of Titanocene Dichloride on Catalyst Activities

Comparisons of H/C atomic ratios of the undoctored and doctored products under various conditions are shown in Figures 6 through 9. In the absence of a catalyst, the oil hydrogenation is very low even under hydrogen pressure. From Figures 6 and 7, H/C atomic ratios of both the undoctored and doctored products treated in the absence of a catalyst deviated in the range close to that of the feed.

Under the $N_2$/catalytic condition (Figure 8), H/C values of both the undoctored and doctored products were almost the same and slowly decreased with temperature. Loss of the volatile components of the oil at higher temperatures was suspected to cause the slight decrease in H/C values. Figure 9 shows that the hydrogenation activity of the catalyst was enhanced with the process temperature from 300 C to 370 C as measured by the increase of H/C values with temperature increase. The effect of titanocene dichloride on the hydrogenation activity of the catalyst was insignificant.

Nitrogen contents of the products are presented in Figures 10 through 13. The nitrogen contents of the products treated in the non-catalytic runs (Figures 10 and 11) appeared to deviate in the range, giving values slightly lower than the nitrogen content in the feed. This indicated that very low nitrogen removal occurred under non-catalytic conditions.

From Figure 12, titanocene dichloride appeared to affect the hydrodenitrogenation activity under the $N_2$/catalytic condition presenting, a trend of decreasing nitrogen contents in the treated oil as a function of temperature. From Figure 13, the hydrodenitrogenation activity of the catalyst was slightly improved at temperatures higher than 350 C with the addition of titanocene dichloride.

From the simulated distillation results, the catalytically hydrotreated products contained high amounts of light initial fractions. The catalyst provided only the activity to convert the very light end of the feed. Pyrolysis appeared to happen in the non-catalytic runs. The products from the non-catalytic runs exhibited very broad boiling distributions due to thermal cracking and polymerization. Titanocene dichloride showed no significant effect on the conversion of oil to lighter fractions.

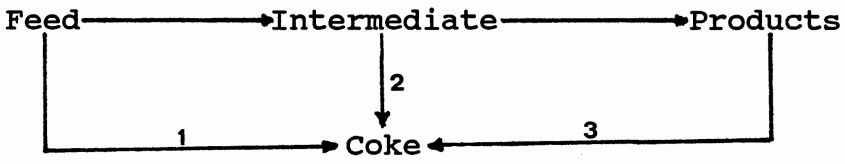
The results of titanium contents in the products are shown in Figure 14. Analysis of the feed showed no titanium content in the feed. Therefore all the titanium measured in the products is those surviving from the added titanium as titanocene dichloride. From Figure 14, complete titanium removal was obtained at temperatures higher than 300 C in the catalytic hydrotreating run (10HCD). For the $N_2$/catalytic run (9NCD), titanium removal was increased with the process temperature and complete titanium removal was obtained at 375 C. In the absence of the catalyst, titanium removal occurred to lower extents. The variations of titanium contents in the treated oils with the process temperature for non-catalytic runs with hydrogen or nitrogen (11HND and 12NND) showed almost similar patterns, with a maximum titanium content in the temperature range of 325 C to 350 C (Figure 14). This behavior was unexpected and can not be explained. However, it appears that a low concentration of titanium left in the product corresponds to a high free radical concentration in the oil sample.

No iron existed in the products from all the catalytic runs, indicating that complete iron removal was achieved with the Shell 324 catalyst. For non-catalytic runs, iron contents in the treated oils were higher than those in the feed. This was obviously due to dissolution and transfer of iron from stainless steel packing pieces into the oil, probably as a result of chlorine action.

In summary, titanocene dichloride had only a small effect on the catalyst activity in this study, whereas it showed significant promoting effects on catalyst activity in Chan's study [1982]. All the processing conditions of this study and his study were similar; however the feedstocks used in these two studies were significantly different. Chan employed a very light SRC oil with the boiling range from 88 C to 199 C and a high oxygen content. Based on the differences in the feedstocks, titanocene dichloride may presumably interact with light fractions of the feedstocks and oxygen compounds resulting in promotion of catalyst activity and reduction of coke formation.

### Effects of Titanocene Dichloride on Catalyst Characteristics

The coke content, pore volume, and surface area of the aged catalysts are given in Table IV. The plots of the coke contents as a function of the reactor section are shown in Figures 15 and 16. Based on the average coke contents as shown in Table IV, titanocene dichloride had no significant effect on the coke formation under either nitrogen or hydrogen atmospheres. However, slightly more coke formed on the catalyst in the nitrogen atmosphere than in the hydrogen atmosphere. Furthermore, there was a distinct difference between coke profiles in hydrogen and nitrogen atmospheres as shown in Figures 15 and 16. The Coke formation along the reactor exhibited two systematically different tendencies: the coke content decreased from top to bottom under the nitrogen atmosphere, and increased from top to bottom under the hydrogen atmosphere. According to the mechanisms of coke formation by a sequence of side reactions [Froment and Bischoff, 1961; 1962], the coke formation under the nitrogen atmosphere was likely generated from precursors in the feed through the side reaction 1, as shown below, while the coke formation under the hydrogen atmosphere was probably generated from some intermediates and products involving the side reactions 2 and 3.



Chan et al. [1982] observed a decreasing coke profile along the reactor in the hydrotreatment runs. Obviously, the coking profile in this study is different from theirs. This suggests that with their particular coal liquid, titanocene dichloride was able to eliminate coke precursors.

From Table IV, the catalyst showed significant loss of pore volume and surface area after the runs. Addition of titanocene dichloride to the feed relatively reduced the loss of catalyst pore volume and surface area. The reduction in the loss of pore volume and surface area of the spent catalyst with the doctored feed was suspected to be due to the deposition of titanium within the catalyst; however, no direct explaination could be given.

Since there was no titanium in the original coal liquid, the titanium on the catalyst came directly from the titanium added to the oil. The titanium distribution within the catalyst pellets withdrawn from different sections of the reactor are shown in Figures 17 and 18. Several titanium profiles within the catalyst under a nitrogen atmosphere (9NCD) were observed along the reactor. As shown in Figure 17, the catalyst from the top section of the reactor from Run 9NCD contained a high penetration of titanium with a center-maximum profile, while edge-maximum profiles of titanium deposits were found in the catalyst from the middle and bottom section of the reactor. This means that in the top section, the organometallic titanium compound penetrated into the catalyst, but it decreased along the reactor, while the solids generated from decomposition or homogeneous reactions of titanocene dichloride were collected on the surface of the catalyst.

The deposition of titanium within the catalyst under hydrotreating condition (Figure 18) showed to be a shell maximum profile with a maximum penetration of titanium into the catalyst being approximately 80 um from the catalyst edge. This indicates that titanocene dichloride reacted with the oil under hydrotreating conditions and formed a different compound which was more reactive with the catalyst and could penetrate into a portion of the radius of the catalyst.

## CONCLUSIONS

The presence of titanocene dichloride in the feedstock increased the formation of free radicals in the entire temperature range of 250 C to 400 C, with rates of recombination and hydrogen capping reactions strongly affecting the concentration of free radicals in the products. The catalyst showed a significant effect on the free radicals, catalyzing their reaction with hydrogen and reducing their concentration. Free radicals appear to be formed by two different mechanisms in the lower (about 250 C) and higher (about 375 C) temperature ranges. Titanocene dichloride appeared to slightly promote HDN at temperatures higher than 350 C. Although no coke suppression was observed with the presence of titanocene dichloride, the loss of catalyst pore volume and surface area was reduced with the doctored feeds. Several profiles of titanium deposit within the spent catalysts were observed along the reactor under the nitrogen atmosphere, whereas the titanium deposit within the catalysts from the hydrotreating runs had a shell-maximum profile. Coke formation on the spent catalysts under hydrogen and nitrogen atmospheres was caused by different coking mechanisms. Two distinctly different coking profiles along the reactor were observed under hydrogen and nitrogen atmospheres.

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## TABLE I

## ANALYSES OF SRC II PROCESS SOLVENT, V 1074

| | |
|---|---|
| Elemental Weight % | |
| Carbon | 86.94 |
| Hydrogen | 11.40 |
| Nitrogen | 0.20 |
| Sulfur | < 0.04 |
| Oxygen | 1.42 |
| Iron | 1.20 ppm |
| Titanium | 0.00 ppm |
| Boiling Distributions by Simulated Distillation | |
| Fraction | Temperature (C) |
| Initial boiling point | 160 |
| 10 % volume | 214 |
| 20 % volume | 237 |
| 30 % volume | 256 |
| 40 % volume | 271 |
| 50 % volume | 288 |
| 60 % volume | 303 |
| 70 % volume | 315 |
| 80 % volume | 338 |
| 90 % volume | 368 |
| End point | 436 |

## TABLE II

## PROPERTIES OF SHELL 324 CATALYST

| | |
|---|---|
| Chemical Composition | |
| | Wt % |
| NiO | 3.4 |
| $MoO_3$ | 19.3 |
| Physical Properties | |
| Geometry | 1.6 mm extrudate |
| Pore Volume | 0.51 $cm^3/g$ |
| Surface area | 202 $m^2/g$ |

# TABLE III

## DESCRIPTIONS OF EXPERIMENTAL CONDITIONS

| | |
|---|---|
| Feed rate | 30 $cm^3/h$ |
| Gas flow rate | 400 $cm^3/min$ (STP) |
| Temperature | 250 C - 400 C (non-catalytic runs) |
| | 300 C - 375 C (catalytic runs) |
| Line-up Period | 1 h (non-catalytic runs) |
| | 2 h (catalytic runs) |
| Pressure | 10.4 MPa |

| Run Name* | Gas Type | Catalyst | Feed |
|---|---|---|---|
| 2NNU** | $N_2$ | None | Undoctored |
| 3HNU | $H_2$ | None | Undoctored |
| 5HCU | $H_2$ | Catalyst | Undoctored |
| 6NNU | $N_2$ | None | Undoctored |
| 7NCU | $N_2$ | Catalyst | Undoctored |
| 8HCU | $H_2$ | Catalyst | Undoctored |
| 9NCD | $N_2$ | Catalyst | Doctored |
| 10HCD | $H_2$ | Catalyst | Doctored |
| 11HND | $N_2$ | None | Doctored |
| 12NND | $N_2$ | None | Doctored |

(Footnotes are in the following page)

## TABLE III (Continued)

## DESCRIPTIONS OF EXPERIMENTAL CONDITIONS

---

* Run numbers are coded to include the consecutive run number and three letters. The first letter is designated for the type of gaseous atmosphere: N for nitrogen and H for hydrogen. The second letter is designated for packing material: N for the non-catalytic and C for the catalytic condition. The last letter is designated for the feedstock: U for the undoctored feedstock and D for the doctored feedstock.

** Run 1 was a test run to evaluate the operation of the reactor. Run 4 was aborted due to an error in added titanium content.

## TABLE IV

## CHARACTERISTICS OF THE AGED CATALYSTS

| Sample | Pore Volume ($cm^3/g$) | Surface Area ($m^2/g$) | Wt % Coke |
|---|---|---|---|
| Fresh | 0.51 | 202 | 0 |
| 5HCU-TOP | 0.25 | 114 | 19.9 |
| 5HCU-MIDDLE | 0.26 | 117 | 22.2 |
| 5HCU-BOTTOM | 0.29 | 124 | 22.4 |
| | Average coke content of three sections | | 21.5 |
| 8HCU-TOP | 0.31 | 147 | 17.6 |
| 8HCU-MIDDLE | 0.26 | 114 | 19.8 |
| 8HCU-BOTTOM | 0.24 | 112 | 24.2 |
| | Average coke content of three sections | | 20.5 |
| 10HCD-TOP | 0.32 | 157 | 18.5 |
| 10HCD-MIDDLE | 0.28 | 129 | 20.0 |
| 10HCD-BOTTOM | 0.30 | 136 | 21.6 |
| | Average coke content of three sections | | 20.0 |

## TABLE IV (Continued)

## CHARACTERISTICS OF THE AGED CATALYSTS

| Sample | Pore Volume ($cm^3/g$) | Surface Area ($m^2/g$) | Wt % Coke |
|---|---|---|---|
| 7NCU-TOP | 0.21 | 106 | 25.5 |
| 7NCU-MIDDLE | 0.24 | 121 | 22.3 |
| 7NCU-BOTTOM | 0.26 | 125 | 20.1 |
| Average coke content of three sections | | | 22.6 |
| 9NCD-TOP | 0.24 | 134 | 24.1 |
| 9NCD-MIDDLE | 0.25 | 136 | 21.6 |
| 9NCD-BOTTOM | 0.26 | 134 | 22.0 |
| Average coke content of three sections | | | 22.6 |

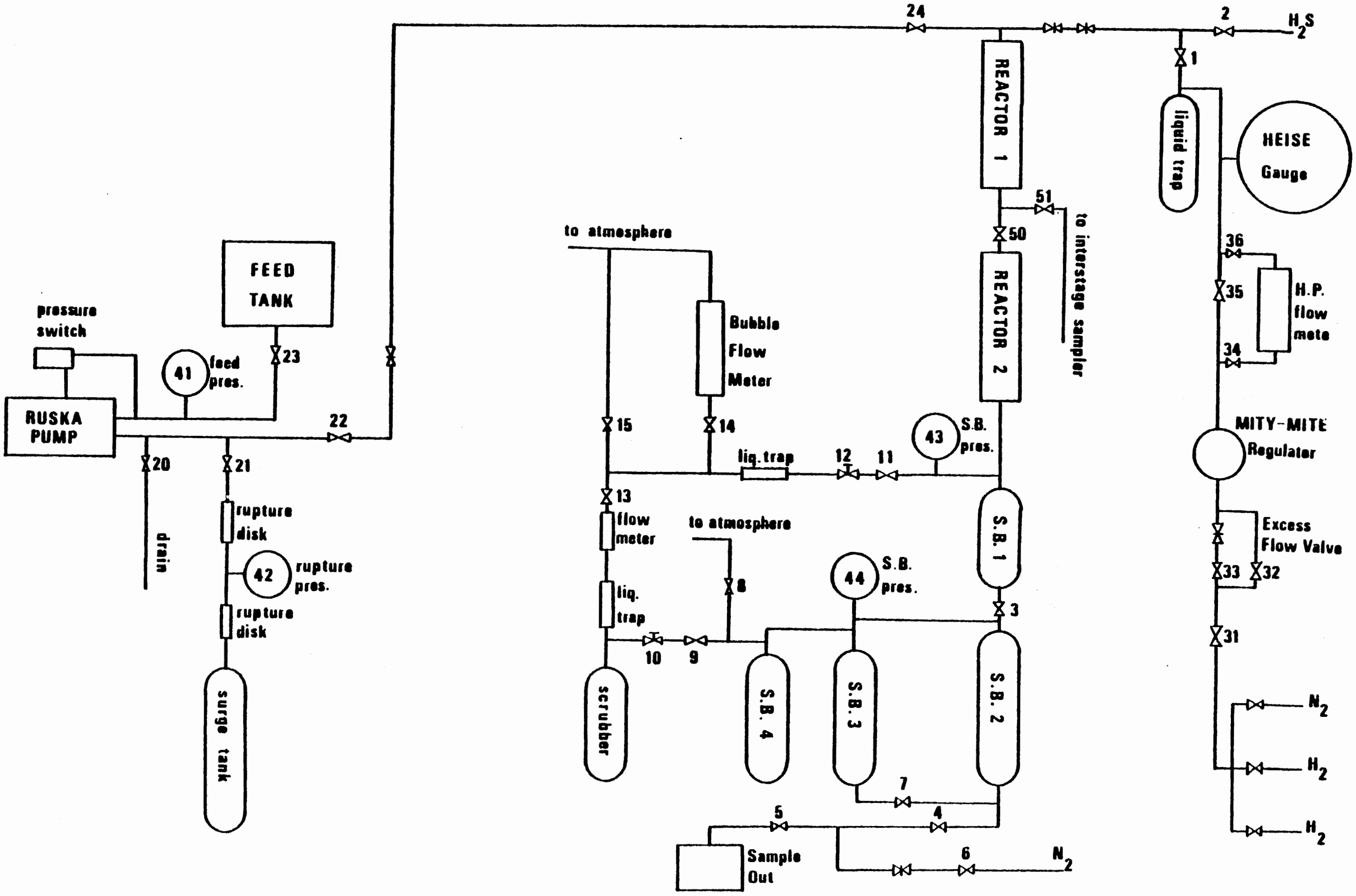

Figure 1. Schematic Diagram of the Reactor System

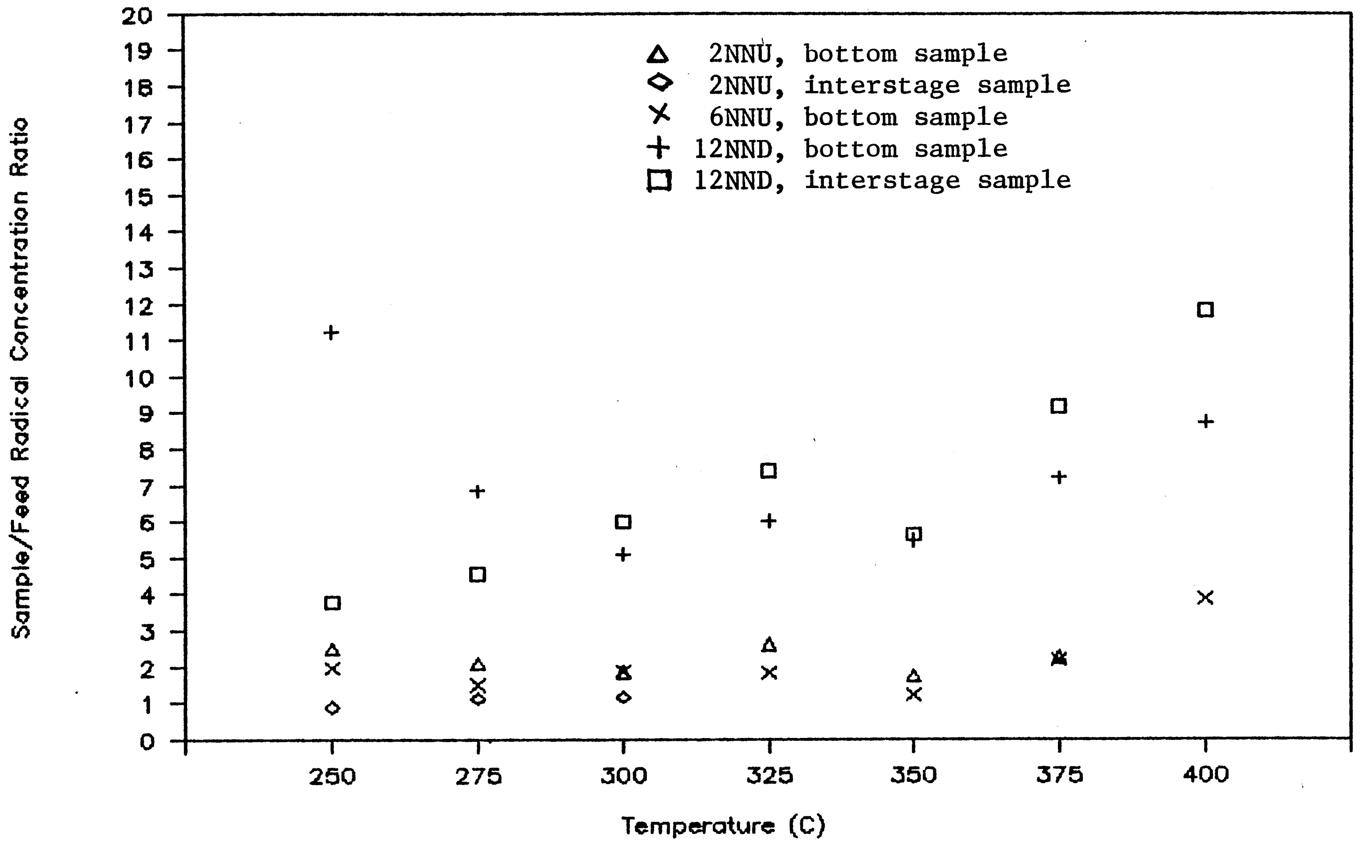

Figure 2. Sample/Feed Radical Concentration Ratio as a Function of Process Temperature under Nitrogen/Non-Catalytic Condition

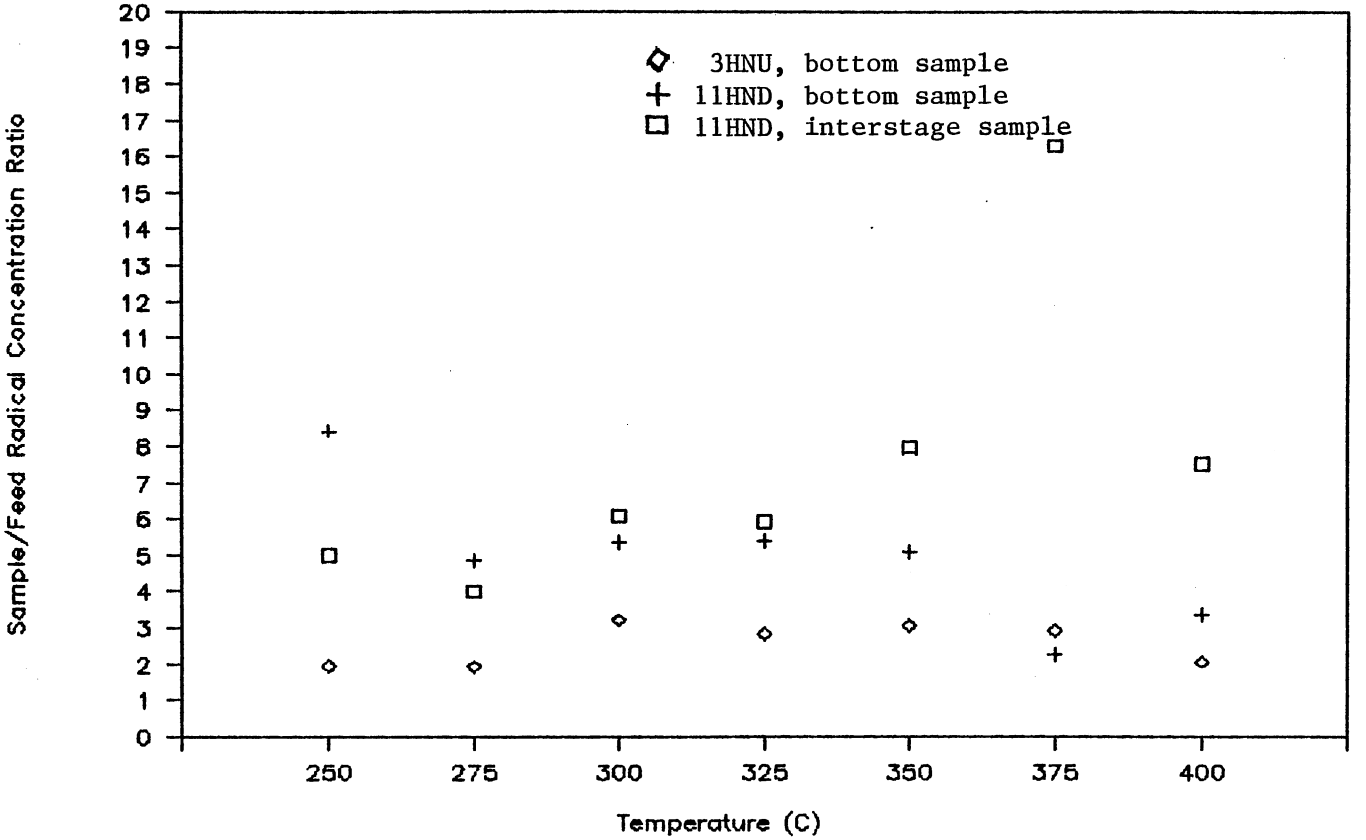

Figure 3. Sample/Feed Radical Concentration Ratio as a Function of Process Temperature under Hydrogen/Non-Catalytic Condition

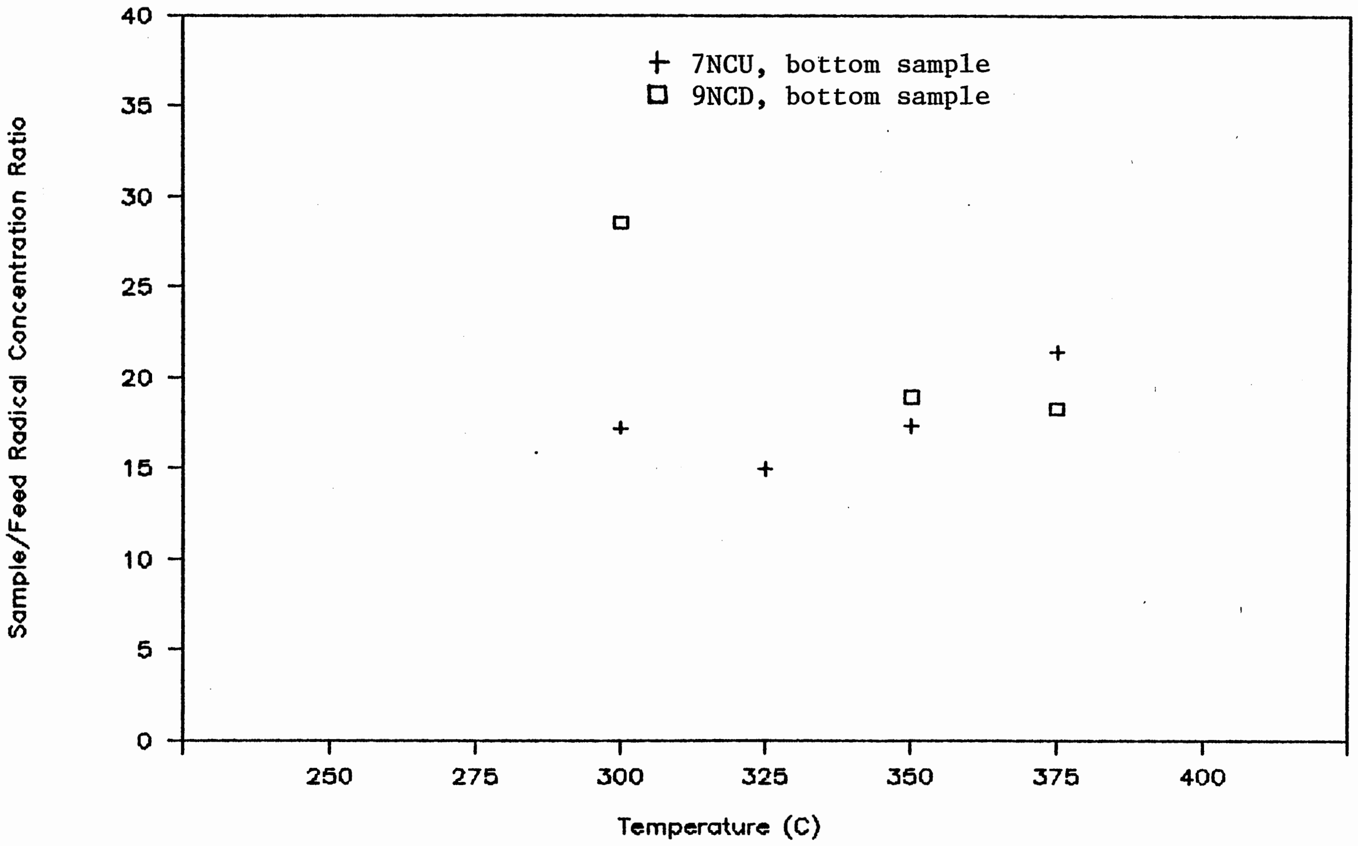

Figure 4. Sample/Feed Radical Concentration Ratio as a Function of Process Temperature under Nitrogen/Catalytic Condition

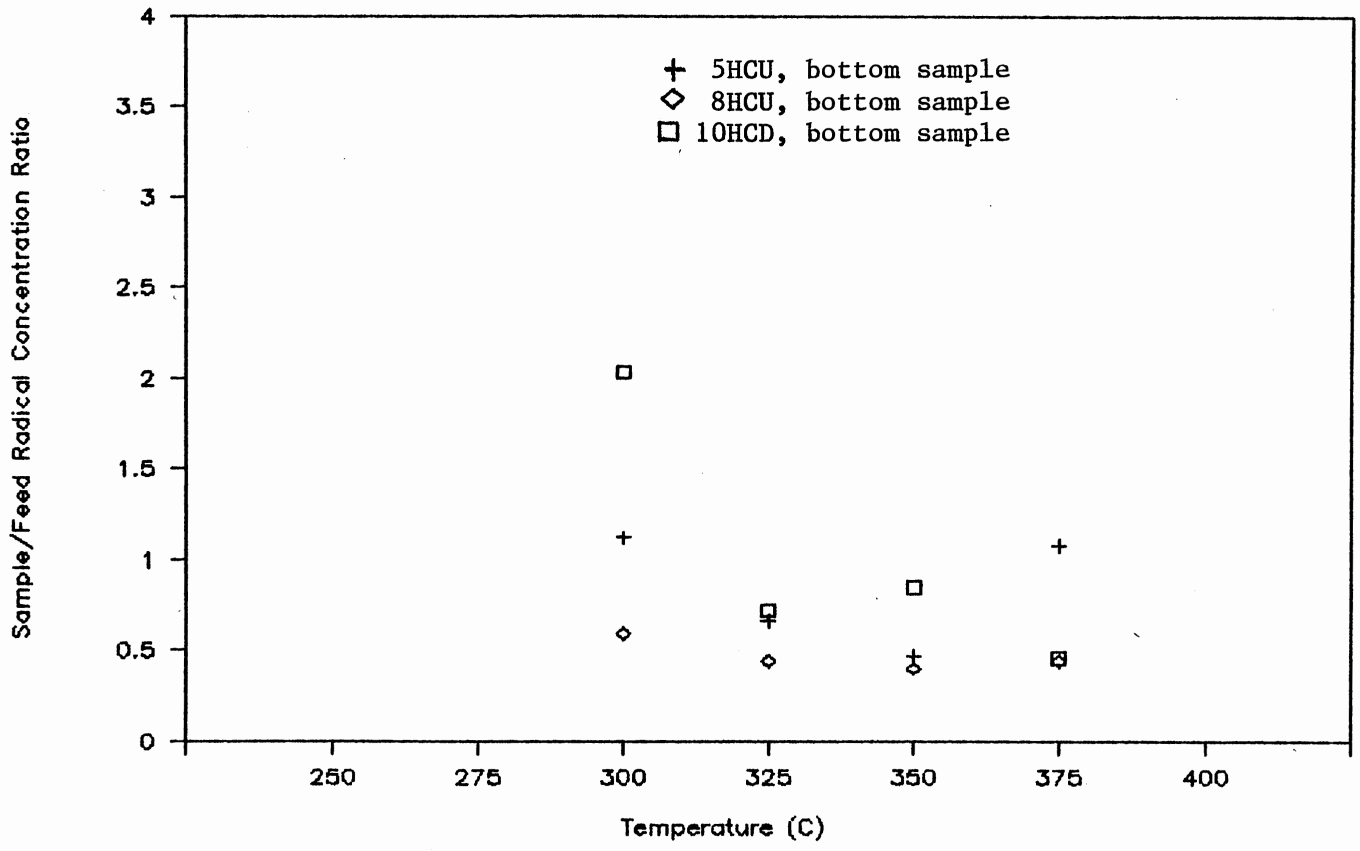

Figure 5. Sample/Feed Radical Concentration Ratio as a Function of Process Temperature under Hydrogen/Catalytic Condition

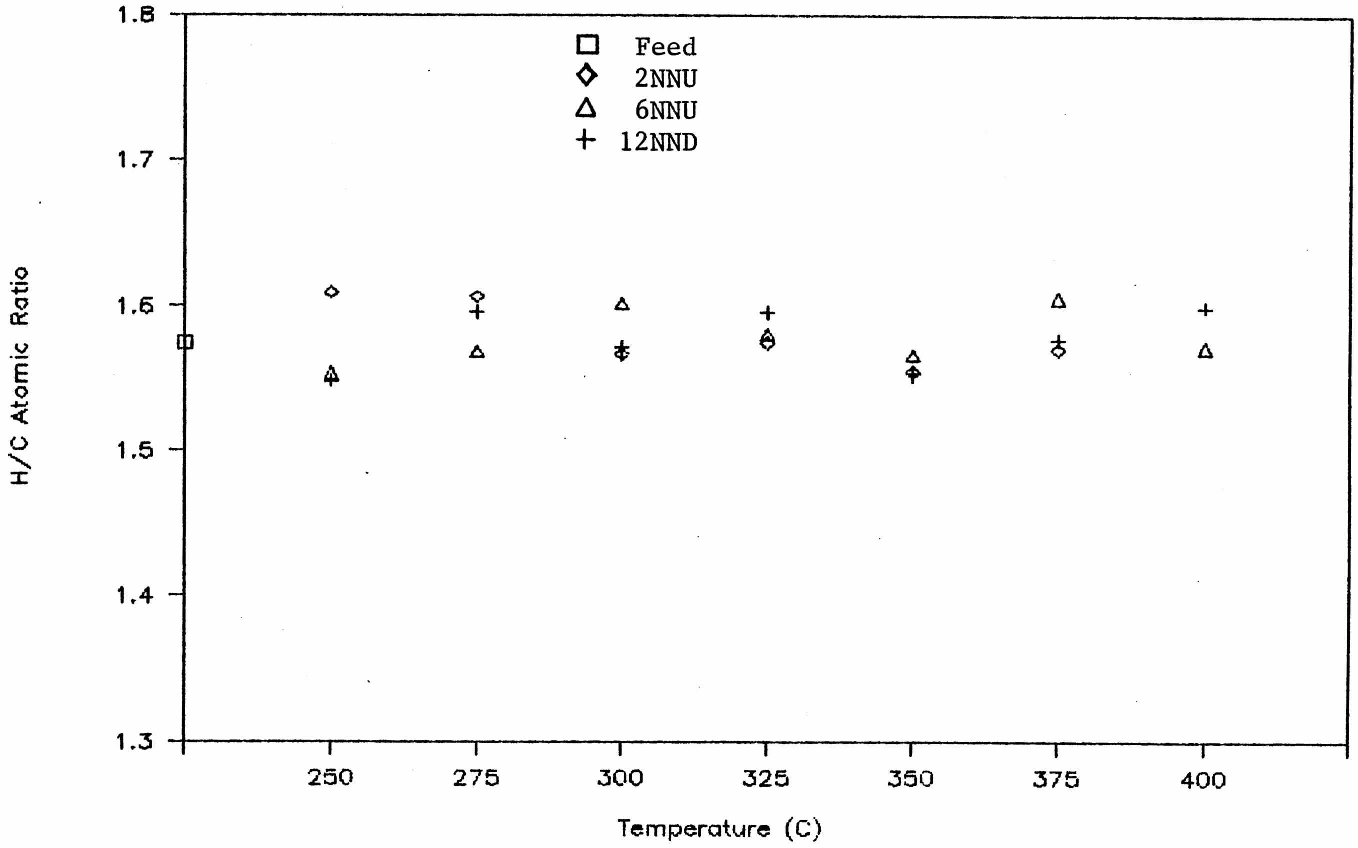

Figure 6. Hydrogenation Activity as a Function of Process Temperature under Nitrogen/Non-Catalytic Condition

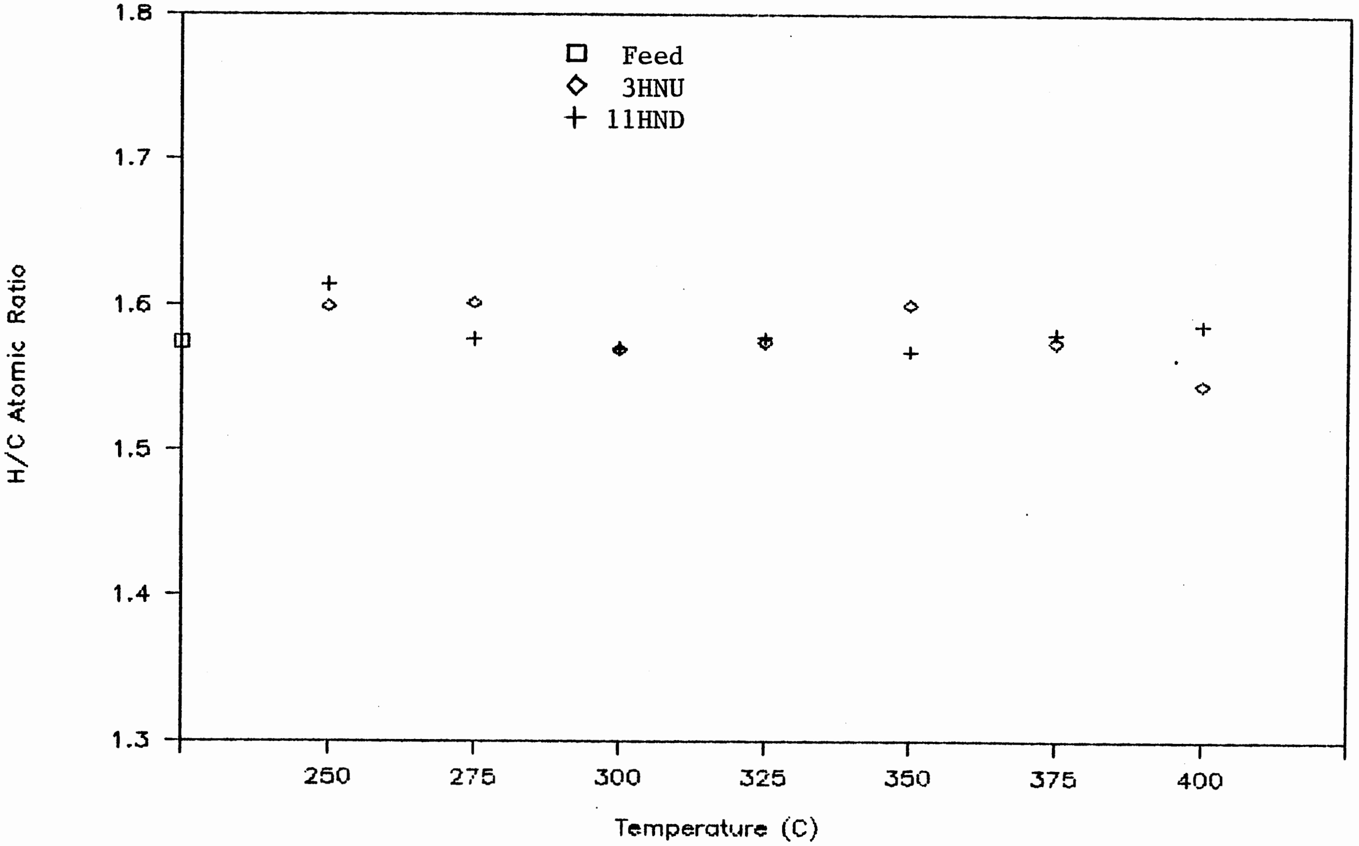

Figure 7. Hydrogenation Activity as a Function of Process Temperature under Hydrogen/Non-Catalytic Condition

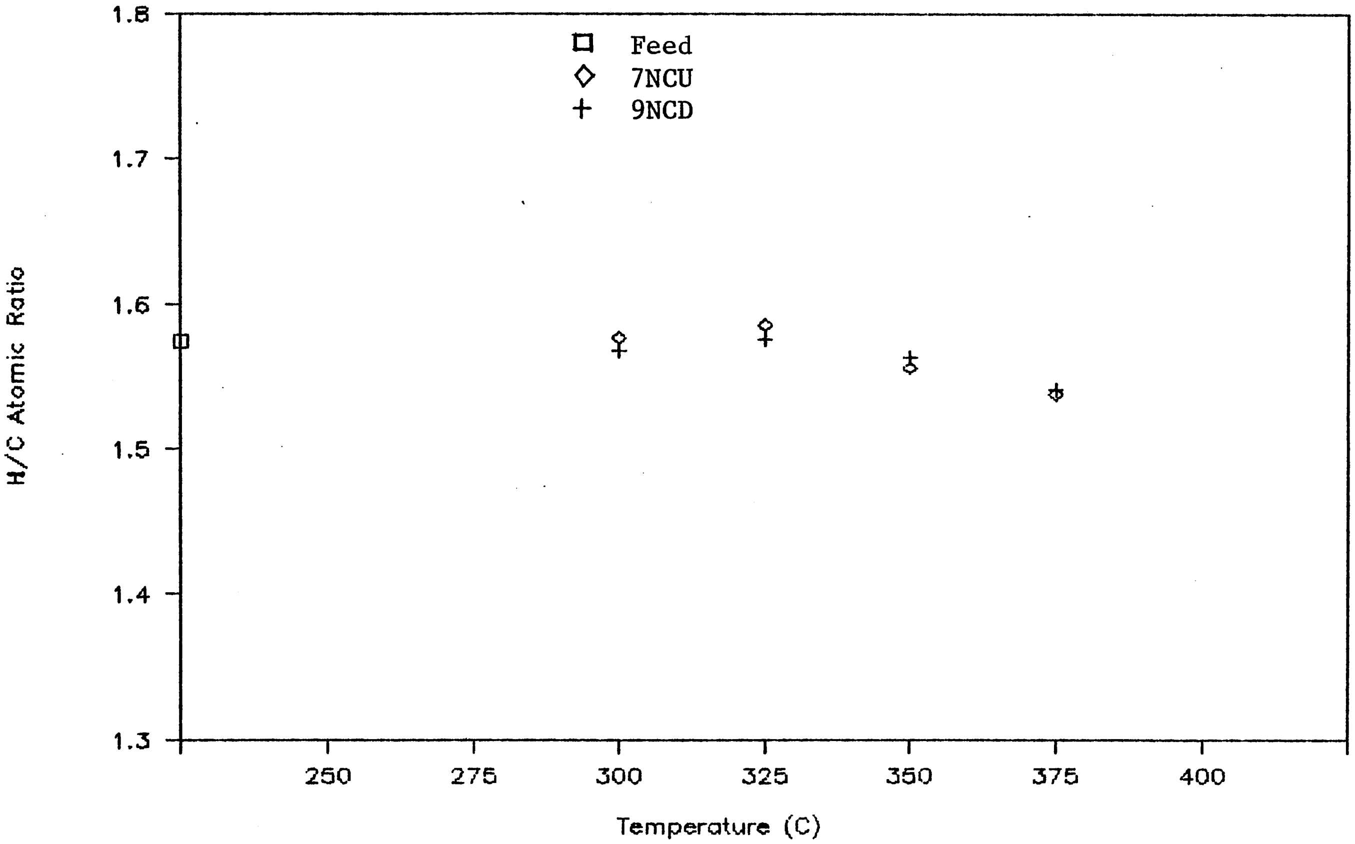

Figure 8. Hydrogenation Activity as a Function of Process Temperature under Nitrogen/Catalytic Condition

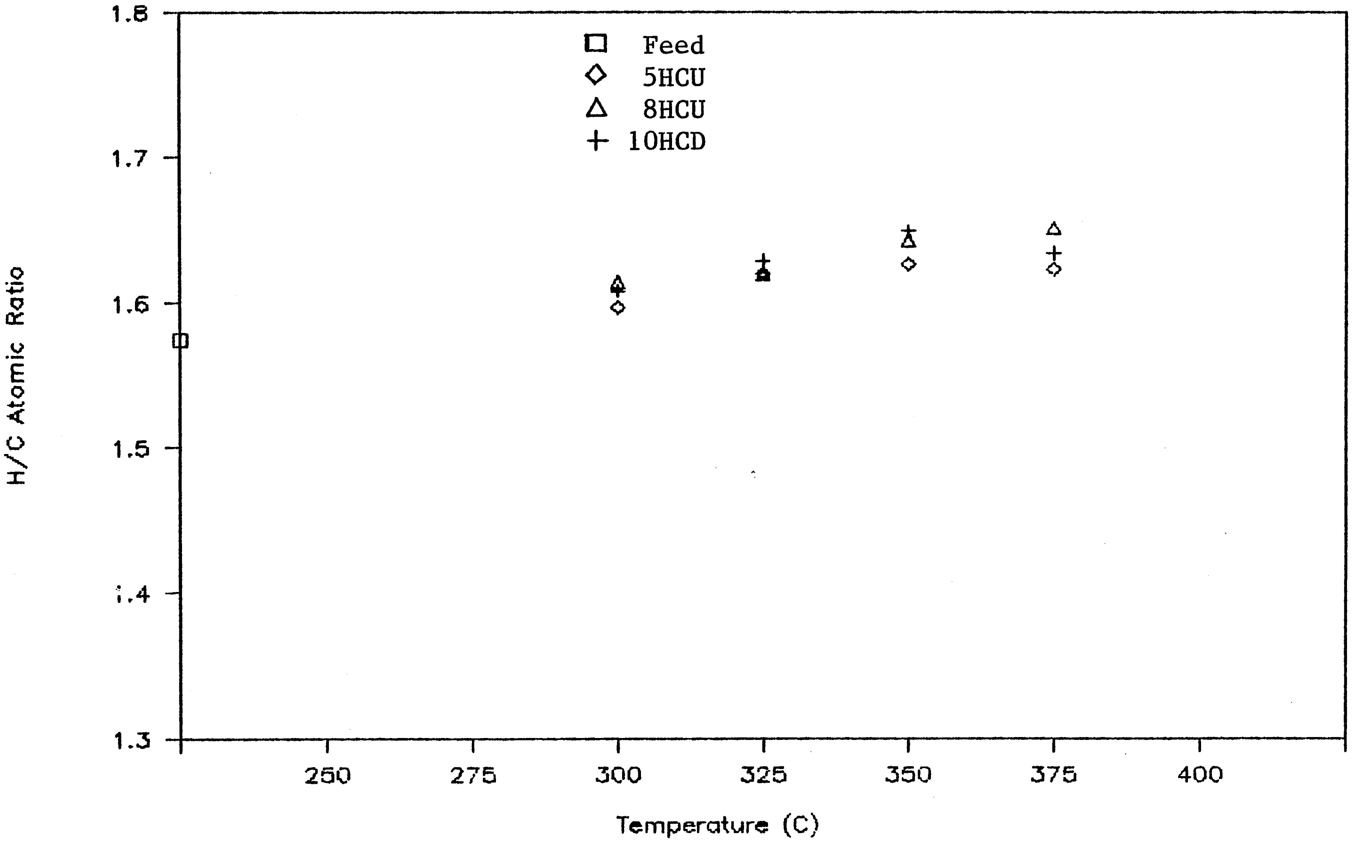

Figure 9. Hydrogenation Activity as a Function of Process Temperature under Hydrogen/Catalytic Condition

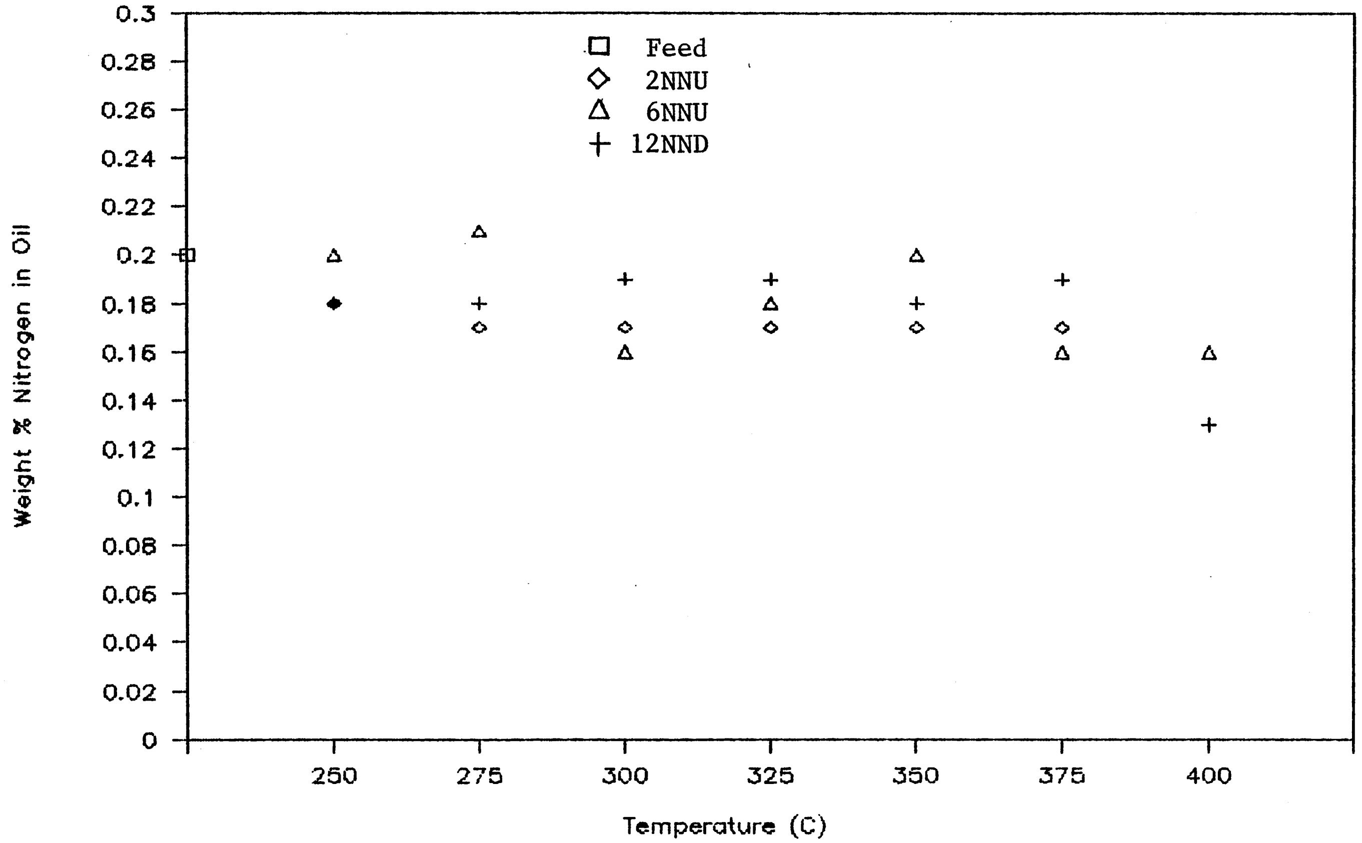

Figure 10. Hydrodenitrogenation Activity as a Function of Process Temperature under Nitrogen/Non-Catalytic Condition

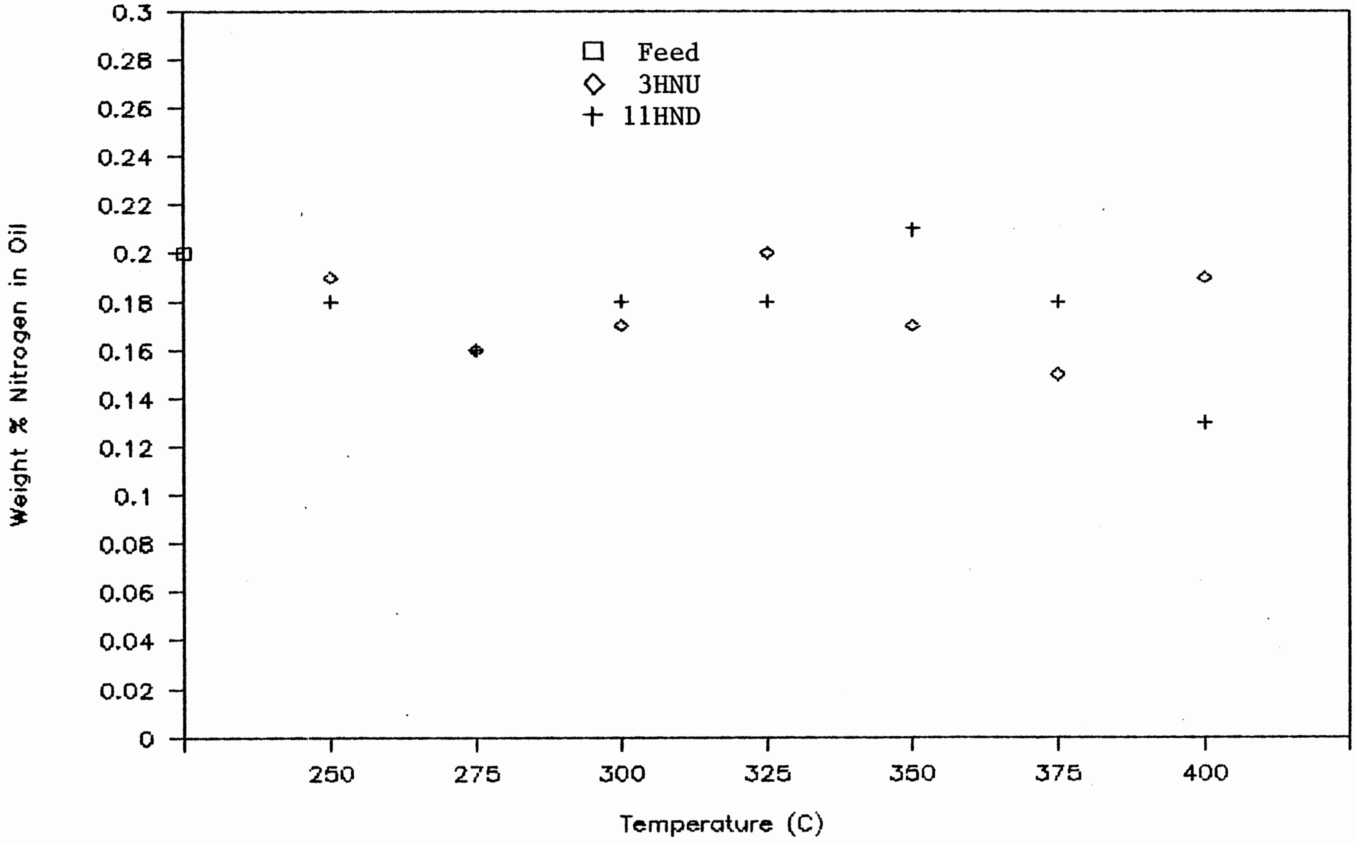

Figure 11. Hydrodenitrogenation Activity as a Function of Process Temperature under Hydrogen/Non-Catalytic Condition

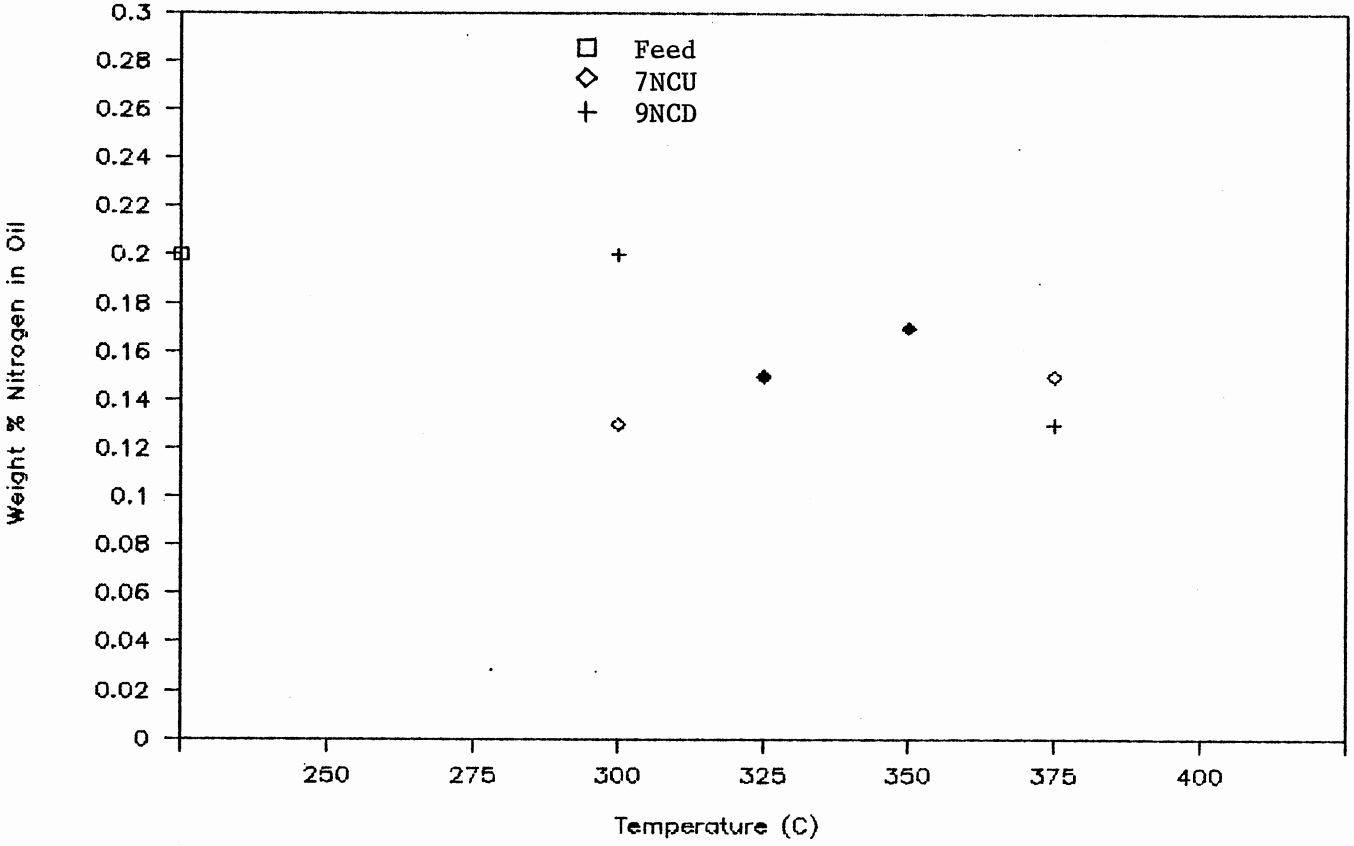

Figure 12. Hydrodenitrogenation Activity as a Function of Process Temperature under Nitrogen/Catalytic Condition

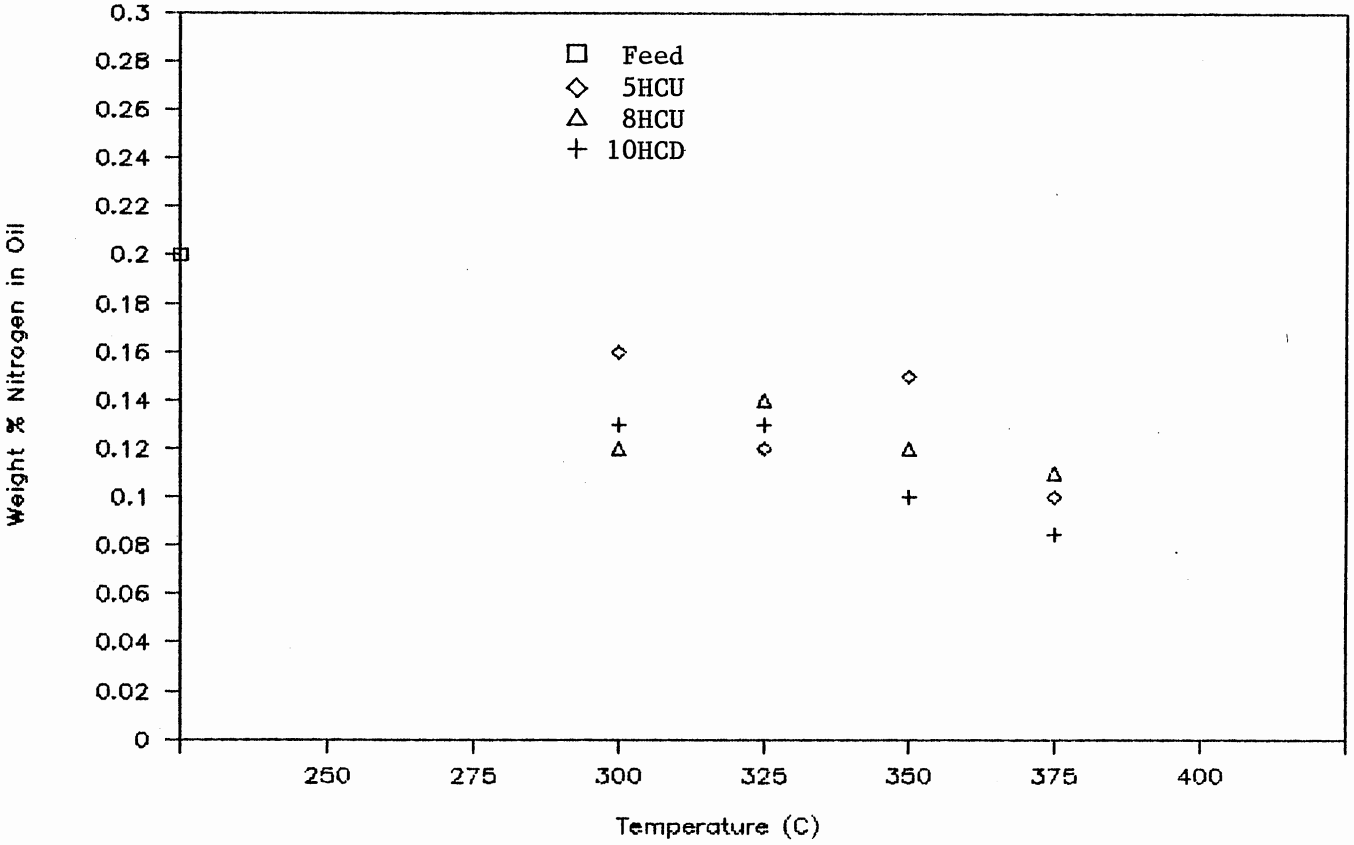

Figure 13. Hydrodenitrogenation Activity as a Function of Process Temperature under Hydrogen/Catalytic Condition

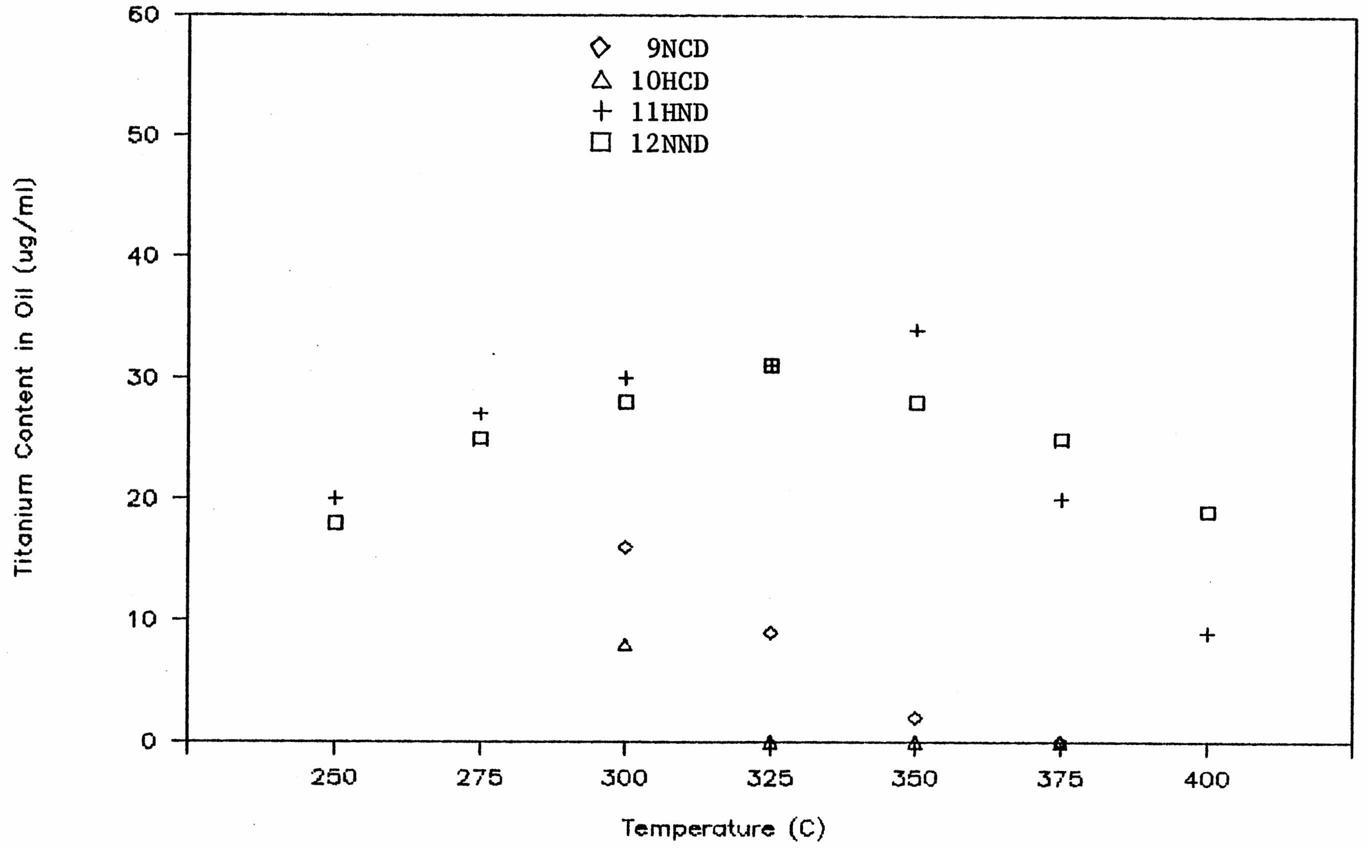

Figure 14. Hydrodemetallation Activity as a Function of Process Temperature under Various Conditions on the Doctored Feedstock

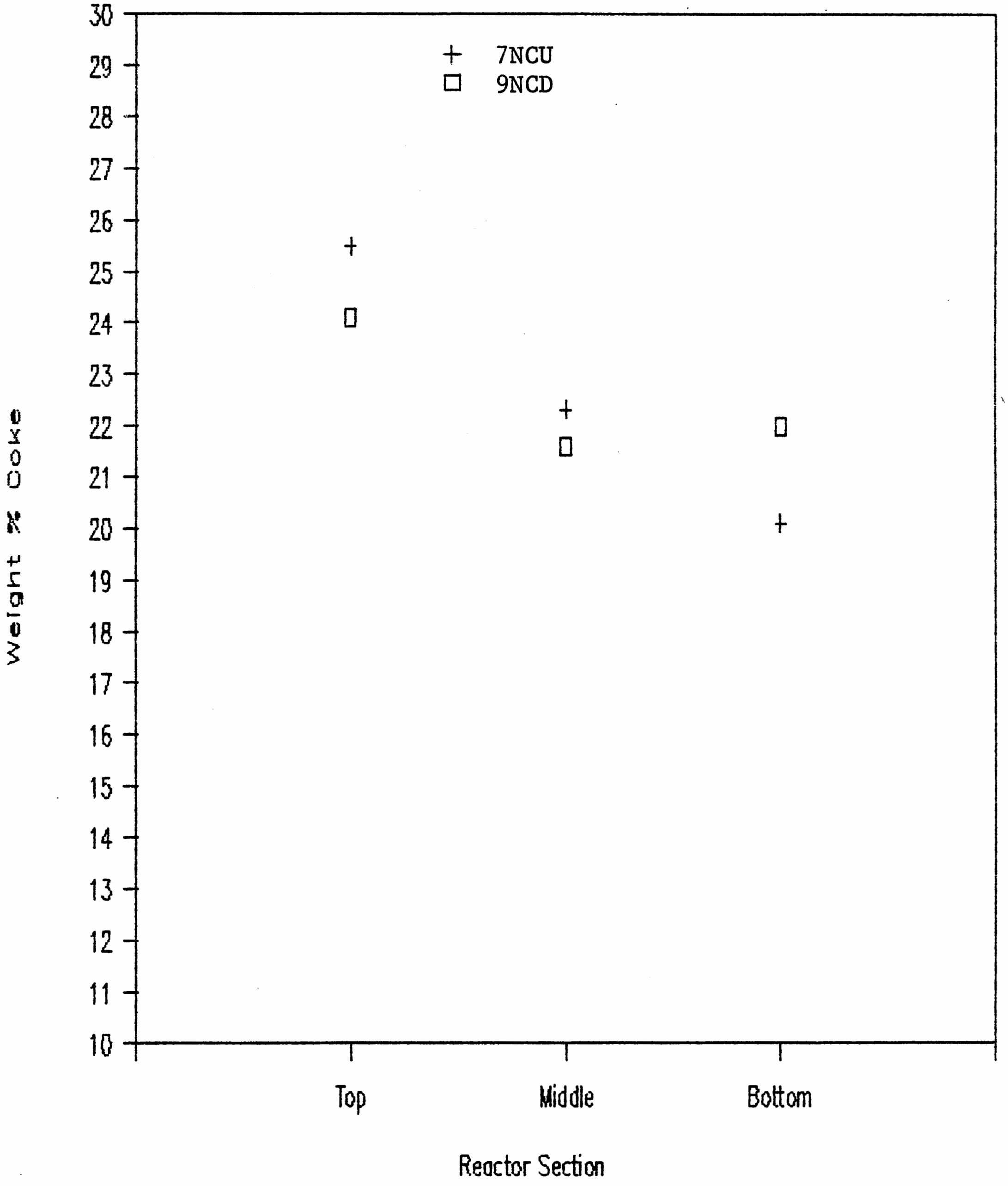

Figure 15. Coke Content as a Function of Reactor Section for Runs under Nitrogen/Catalytic Condition

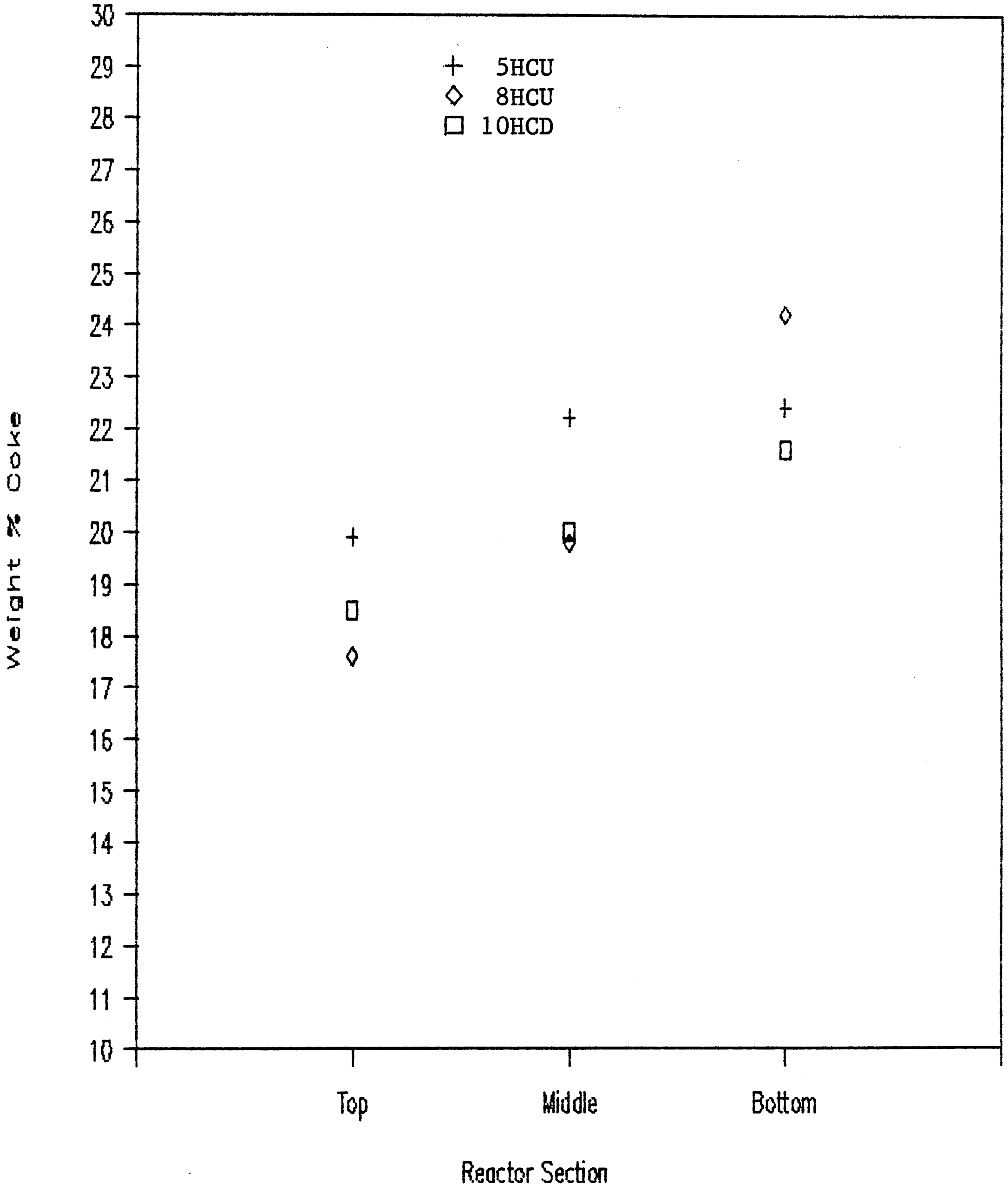

Figure 16. Coke Content as a Function of Reactor Section for Runs under Hydrogen/Catalytic Condition

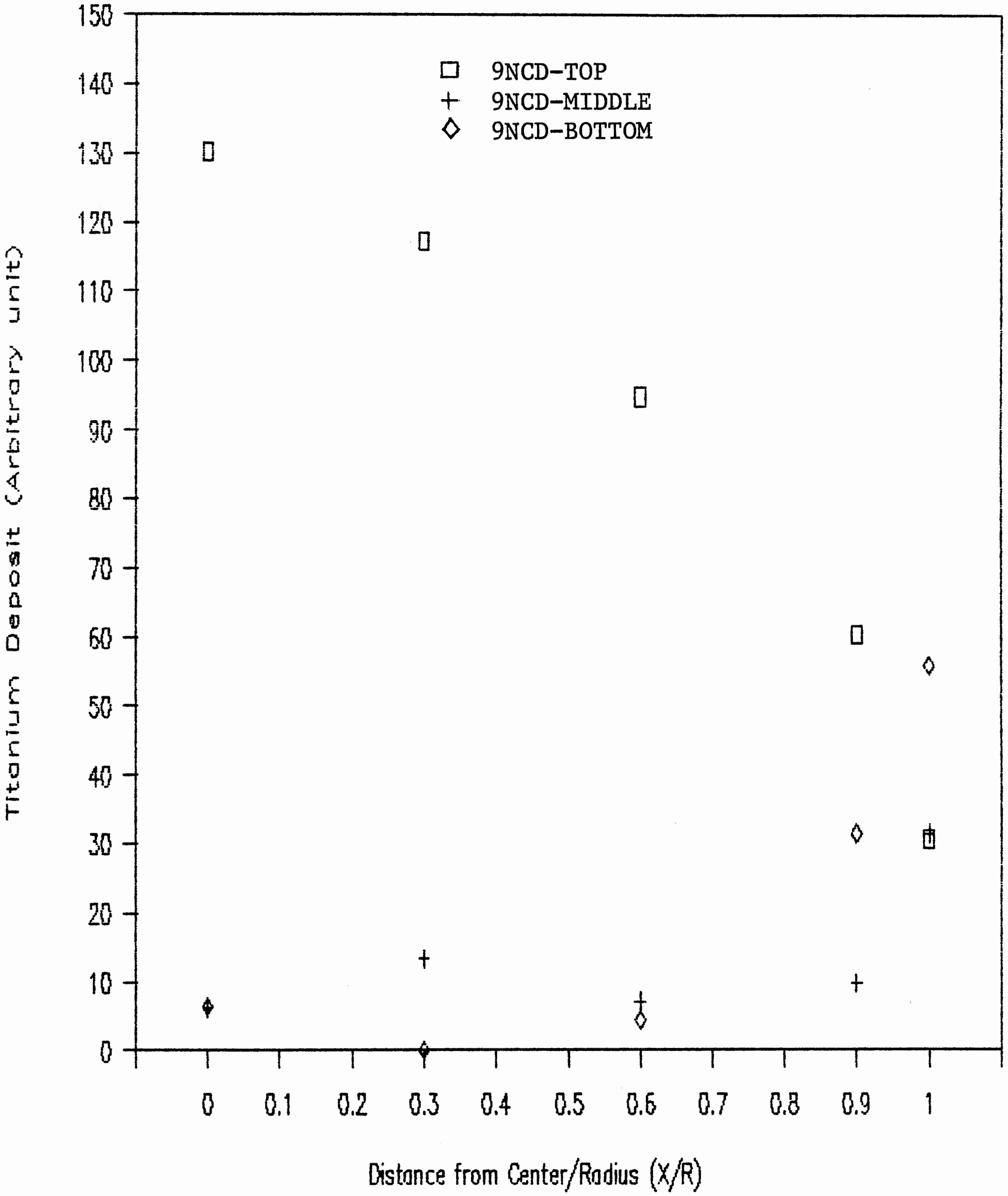

Figure 17. Titanium Deposit Distribution along Cross-Section of Catalyst Pellet Withdrawn from Run under Nitrogen/Catalytic Condition

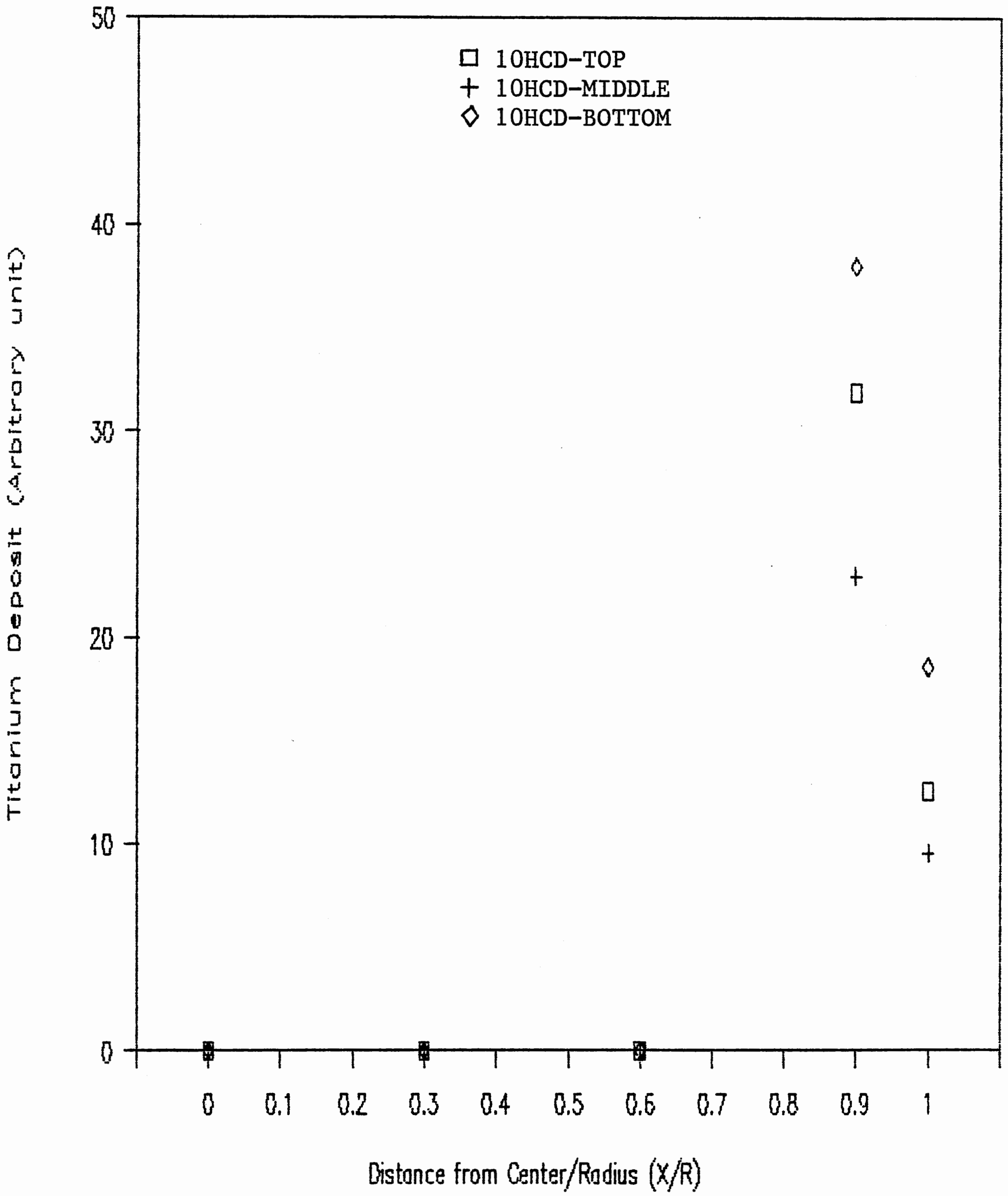

Figure 18. Titanium Deposit Distribution along Cross-Section of Catalyst Pellet Withdrawn from Run under Hydrogen/Catalytic Condition

# CHAPTER III

# CONCLUSIONS AND RECOMMENDATIONS

## CONCLUSIONS

Several conclusions can be drawn from the observations of this study.

1. The free radical formation in a coal-derived liquid during various treatments is controlled by the process conditions of temperature, the type of gaseous atmosphere, and the presence of the catalyst.

2. Titanocene dichloride increases the free radical formation, however, the concentrations of free radicals were dependent on the process conditions.

3. Titanocene dichloride slightly promotes the HDN activity of the catalyst in the temperature range of 350 C to 375 C.

4. The different coke formation tendencies along the reactor under nitrogen and hydrogen atmospheres are caused by different coking mechanisms.

5. Titanocene dichloride reduces the loss of catalyst pore volume and surface area of the aged catalyst.

6. The titanium deposition within the aged catalyst under the hydrotreating condition is a shell maximum pattern.

## RECOMMENDATIONS

Several recommendations can be proposed for further studies:

1. The study of free radical formation during

treatments should be done in an insitu reactor system to obtain more informative knowledge of free radicals. Since the life-time of some reactive radicals is very short, they may interact with each other and with other radicals during the period of sample collection before being frozen in liquid nitrogen.

2. In future studies of free radical formation in the trickle-bed reactor system, instantaneous samples should be collected from the interstage sampling device. However, some problems in collecting samples can be solved by allowing longer collection period to eliminate evaporation problem and practicing the sample taking procedure to keep a precise collection period.

3. Besides monitoring the products and characterization of the aged catalysts, the effects of titanocene dichloride should be investigated on the hydrotreating activity of the aged catalysts on some model compounds of S, N, and O. This will provide knowledge of the effect of coke and Ti deposits within the aged catalyst from the doctored feedstock on the hydrotreating activity.

4. In this study, titanocene dichloride exhibits to affect free radical formation, while its effect on catalyst activity and deactivation could slightly be observed. Since titanocene dichloride exhibited significant improvements on the hydrotreating of an SRC light oil, another set of experiments on the free radical

formation should be conducted on the SRC light oil, if available. This may provide better knowledge of free radical formation related to the effect of titanocene dichloride on catalyst activity and deactivation.

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# APPENDIX A

# RESULTS OF ELECTRON SPIN RESONANCE SPECTROSCOPY

# RESULTS OF ELECTRON SPIN RESONANCE (ESR) SPECTROSCOPY

Electron Spin Resonance (ESR) spectroscopy is an analytical technique which utilizes molecular absorption spectrum to provide information of paramagnetic species. In the ESR experiments, a microwave beam is irradiated through a sample in an appropriate cavity system placed in a homogeneous magnetic field. The absorption condition is fulfilled by varying the magnetic field strength to meet the transitional energy levels of paramagnetic species in the sample. Since a free radical which is a molecule containing one unpaired electron is one of the paramagnetic species, ESR is an appropriate tool to study free radicals contained in coal-derived samples.

The ESR measurement obtained from a recorder is usually presented in the form of first derivative absorption spectrum as a function of magnetic field. Some examples of the spectra are presented in Figure 19. Basically, several parameters can be obtained from an ESR signal to indicate the characteristics of free radicals in the sample. They include g-value, free radical concentration or intensity, signal line width, signal line shape. However, only two ESR parameters of the free radical concentration and the g-value are studied in this work, since they are among the most informative parameters to monitor the behavior of free radicals.

g-value : This parameter indicates the position of the resonant condition and can be calculated by:

$$g = hf/BH$$

where h is the Planck 's constant ($6.62620 \times 10^{-27}$ erg sec)

f is the resonant frequency (Hz)

B is the Bohr magneton (9.27410 erg $G^{-1}$)

H is the resonant magnetic field (G)

Free radical concentration : Basically, the radical concentration is proportional to the double integration area of the first derivative signal. However, one must be aware of the saturation characteristic of the ESR signals. This involves the level of microwave power used in the experiments. At low microwave powers, the ESR signal varies linearly as a function of the microwave field strength. However, when microwave powers are sufficiently high and reach the saturation level, the variation of signal with microwave field is no longer linear. The observation of changes in free radical concentration under saturation conditions is then invalid. In this study, a microwave power of 200 uW was employed in the experiments. Experiments with varying microwave power have indicated that a microwave power of 200 uW is sufficiently low to give the linear signals [Silbernagel et al., 1986].

The free radical concentration is presented in the dimensionless form by values of gamma. The gamma is defined as:

$$\text{gamma} = \frac{\text{The double integration area of the sample signal}}{\text{The double integration area of the feed signal}}$$

All the ESR measurements were conducted at room temperature. In the ESR experiments, a sample which was previously frozen in liquid nitrogen was allowed to liquefy in the ESR cavity at ambient condition. Then, the measurement was immediately taken. Several preliminary measurements of the feedstock at 77 K (in liquid nitrogen) showed inconsistent and random results. The frozen samples contained cracks and air gaps which resulted in inconsistent and small signals. However, after melting, multiple measurements of the liquid samples at room temperature demonstrated good reproducibility.

For the results of the double integration area calculated by a Hewlett Packard Personal Computer, multiple calculations of some signals showed very good reproducibility within 3 significant digits. The g-values are accurate enough to be given up to the fourth digit after the decimal point. For all the ESR measurements the gamma and g-value obtained in this study are tubulated in Table V.

## TABLE V

## RESULTS OF ELECTRON SPIN RESONANCE SPECTROSCOPY

| Sample | Gamma | g-value |
|---|---|---|
| Feed (V 1074) | 1.00 | 2.0028 |
| 2NNU-1-250 interstage | 0.89 | 2.0027 |
| 2NNU-2-275 interstage | 1.11 | 2.0028 |
| 2NNU-3-300 interstage | 1.16 | 2.0027 |
| 2NNU-1-250 | 2.49 | 2.0025 |
| 2NNU-2-275 | 2.09 | 2.0025 |
| 2NNU-3-300 | 1.85 | 2.0024 |
| 2NNU-4-325 | 2.59 | 2.0024 |
| 2NNU-5-350 | 1.74 | 2.0023 |
| 2NNU-6-375 | 2.24 | 2.0024 |
| 3HNU-1-250 | 1.93 | 2.0025 |
| 3HNU-2-275 | 1.92 | 2.0026 |
| 3HNU-3-300 | 3.20 | 2.0025 |
| 3HNU-4-325 | 2.82 | 2.0025 |
| 3HNU-5-350 | 3.06 | 2.0025 |
| 3HNU-6-375 | 2.92 | 2.0026 |
| 3HNU-7-400 | 2.04 | 2.0026 |

TABLE V (Continued)

| Sample | Gamma | g-value |
|---|---|---|
| 5HCU-1-300 | 1.12 | 2.0026 |
| 5HCU-2-325 | 0.66 | 2.0026 |
| 5HCU-3-350 | 0.47 | 2.0026 |
| 5HCU-4-375 | 1.08 | 2.0026 |
| 6NNU-1-250 | 1.96 | 2.0026 |
| 6NNU-2-275 | 1.51 | 2.0027 |
| 6NNU-3-300 | 1.88 | 2.0026 |
| 6NNU-4-325 | 1.83 | 2.0026 |
| 6NNU-5-350 | 1.21 | 2.0027 |
| 6NNU-6-375 | 2.19 | 2.0027 |
| 6NNU-7-400 | 3.86 | 2.0027 |
| 7NCU-1-300 | 17.2 | 2.0025 |
| 7NCU-2-325 | 15.0 | 2.0025 |
| 7NCU-3-350 | 17.4 | 2.0025 |
| 7NCU-4-375 | 21.4 | 2.0025 |

TABLE V (Continued)

| Sample | Gamma | g-value |
|---|---|---|
| 8HCU-1-300 | 0.59 | 2.0027 |
| 8HCU-2-325 | 0.44 | 2.0027 |
| 8HCU-3-350 | 0.40 | 2.0027 |
| 8HCU-4-375 | 0.44 | 2.0027 |
| 9NCD-1-300 | 28.5 | 2.0025 |
| 9NCD-2-325* | - | - |
| 9NCD-3-350 | 18.9 | 2.0025 |
| 9NCD-4-375 | 18.2 | 2.0026 |
| 10HCD-1-300 | 2.03 | 2.0027 |
| 10HCD-2-325 | 0.72 | 2.0026 |
| 10HCD-3-350 | 0.85 | 2.0027 |
| 10HCD-4-375 | 0.46 | 2.0027 |

* The 9NCD-2-325 sample tube was broken.

TABLE V (Continued)

| Sample | Gamma | g-value |
|---|---|---|
| 11HND-1-250 interstage | 5.00 | 2.0025 |
| 11HND-2-275 interstage | 3.99 | 2.0026 |
| 11HND-3-300 interstage | 6.08 | 2.0025 |
| 11HND-4-325 interstage | 5.92 | 2.0025 |
| 11HND-5-350 interstage | 7.98 | 2.0025 |
| 11HND-6-375 interstage | 16.3 | 2.0024 |
| 11HND-7-400 interstage | 7.53 | 2.0024 |
| 11HND-1-250 | 8.42 | 2.0025 |
| 11HND-2-275 | 4.87 | 2.0025 |
| 11HND-3-300 | 5.34 | 2.0025 |
| 11HND-4-325 | 5.39 | 2.0025 |
| 11HND-5-350 | 5.08 | 2.0025 |
| 11HND-6-375 | 2.24 | 2.0026 |
| 11HND-7-400 | 3.35 | 2.0026 |

TABLE V (Continued)

| Sample | Gamma | g-value |
|---|---|---|
| 12NND-1-250 interstage | 3.77 | 2.0024 |
| 12NND-2-275 interstage | 4.54 | 2.0024 |
| 12NND-3-300 interstage | 5.99 | 2.0024 |
| 12NND-4-325 interstage | 7.38 | 2.0024 |
| 12NND-5-350 interstage | 5.63 | 2.0024 |
| 12NND-6-375 interstage | 9.16 | 2.0024 |
| 12NND-7-400 interstage | 11.8 | 2.0024 |
| 12NND-1-250 | 11.2 | 2.0024 |
| 12NND-2-275 | 6.83 | 2.0024 |
| 12NND-3-300 | 5.10 | 2.0024 |
| 12NND-4-325 | 6.00 | 2.0024 |
| 12NND-5-350 | 5.48 | 2.0024 |
| 12NND-6-375 | 7.19 | 2.0024 |
| 12NND-7-400 | 8.73 | 2.0024 |

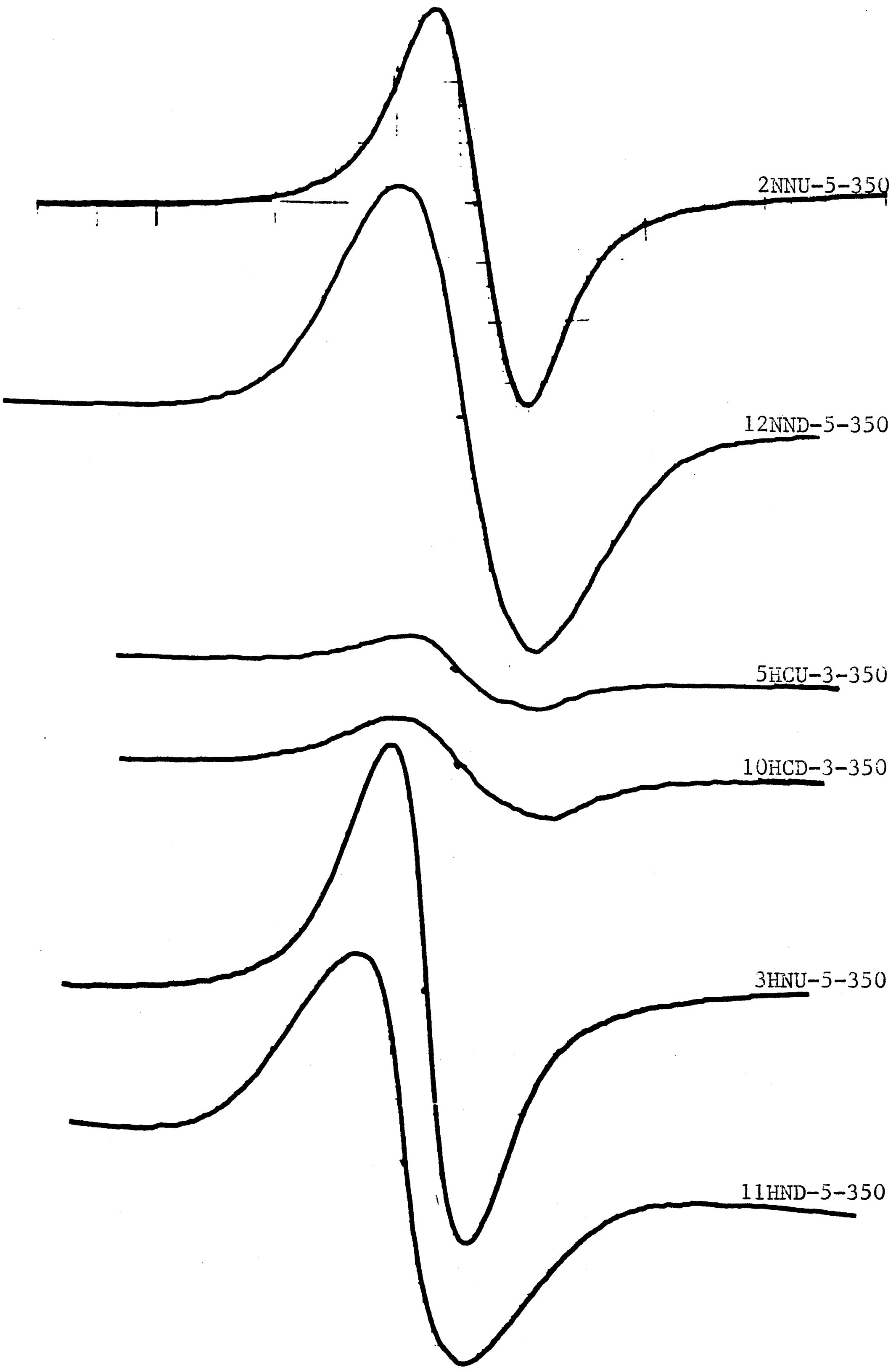

Figure 19. Electron Spin Resonance First Derivative Absorption Spectra

# APPENDIX B

# RESULTS OF ELEMENTAL ANALYSIS

## RESULTS OF ELEMENTAL ANALYSIS

All the results of elemental analyses are given in Table VI where the contents of Ti and Fe are reported in ug/ml, and those of N, C, H, and O (by balance) are reported in weight percentages. Since the S content in all the products is lower than the detection limit (< 0.04 weight % S) of the instrument, no composition of S is reported.

In N, C, and H analysis by a Perkin Elmer Model 240B, pyridine is used as a calibration standard for the signal to weight ratio constants ($K_N$, $K_C$, and $K_H$). It was found that these constants were dependent on the sample size of the standard. To obtain accurate results, several sample sizes of the standard were used to establish the correlation between the constants and the sample size. Then, the K contants used for the feed and product samples were calibrated from correlation for each K. In this study, the sample sizes of pyridine ranging from 1600 ug to 2000 ug were used for the calibration since the sample sizes of the feed and products were prepared in this weight range.

For the catalytically hydrotreated samples (5HCU, 8HCU, 10HCD), several measurements were employed to maintain the accuracy of the results. The results showed maximum variations of 0.03 weight % for N, 0.35 weight % for C, and 0.25 weight % for H.

# TABLE VI

# RESULTS OF ELEMENTAL ANALYSIS

| | Wt % | | | | ug/ml | |
|---|---|---|---|---|---|---|
| Sample | N | C | H | O by difference | Ti | Fe |
| Feed(V 1074) | 0.20 | 86.94 | 11.40 | 1.46 | 0.0 | 1.2 |
| 2NNU-1-250 | 0.18 | 87.10 | 11.68 | 1.04 | 0.0 | 14.6 |
| 2NNU-2-275 | 0.17 | 87.13 | 11.66 | 1.06 | 0.0 | 15.6 |
| 2NNU-3-300 | 0.17 | 87.35 | 11.40 | 1.08 | 0.0 | 16.0 |
| 2NNU-4-325 | 0.17 | 86.51 | 11.35 | 1.97 | 0.0 | 15.4 |
| 2NNU-5-350 | 0.17 | 87.00 | 11.27 | 1.56 | 0.0 | 16.0 |
| 2NNU-6-375 | 0.17 | 87.72 | 11.48 | 0.63 | 0.0 | 16.2 |
| 3HNU-1-250 | 0.19 | 86.99 | 11.59 | 1.23 | 0.0 | 13.8 |
| 3HNU-2-275 | 0.16 | 87.02 | 11.61 | 1.21 | 0.0 | 13.2 |
| 3HNU-3-300 | 0.17 | 87.28 | 11.41 | 1.14 | 0.0 | 13.2 |
| 3HNU-4-325 | 0.20 | 87.28 | 11.51 | 0.55 | 0.0 | 5.4 |
| 3HNU-5-350 | 0.17 | 87.01 | 11.60 | 1.22 | 0.0 | 3.1 |
| 3HNU-6-375 | 0.15 | 86.97 | 11.41 | 1.47 | 0.0 | 4.0 |
| 3HNU-7-400 | 0.19 | 87.44 | 11.26 | 1.11 | 0.0 | 2.0 |

TABLE VI (Continued)

| | Wt % | | | | ug/ml | |
|---|---|---|---|---|---|---|
| Sample | N | C | H | O by difference | Ti | Fe |
| 5HCU-1-300(12) | 0.14 | 86.47 | 11.59 | 1.80 | 0.0 | 0.0 |
| 5HCU-2-300(24) | 0.12 | 87.01 | 11.56 | 1.31 | 0.0 | 0.0 |
| 5HCU-3-300(32) | 0.12 | 86.50 | 11.39 | 1.99 | 0.0 | 0.0 |
| 5HCU-4-300(36) | 0.16 | 86.63 | 11.52 | 1.69 | 0.0 | 0.0 |
| 5HCU-5-300* | - | - | - | - | 0.0 | 0.0 |
| 5HCU-6-325 | 0.12 | 86.64 | 11.70 | 1.54 | 0.0 | 0.0 |
| ** +/- | 0.02 | 0.22 | 0.14 | 0.29 | | |
| 5HCU-7-350 | 0.15 | 87.11 | 11.81 | 0.94 | 0.0 | 0.0 |
| ** +/- | 0.01 | 0.20 | 0.25 | 0.38 | | |
| 5HCU-8-375 | 0.10 | 87.03 | 11.77 | 1.14 | 0.0 | 0.0 |
| ** +/- | 0.02 | 0.16 | 0.13 | 0.12 | | |
| 6NNU-1-250 | 0.20 | 86.17 | 11.15 | 2.48 | 0.0 | 0.2 |
| 6NNU-2-275 | 0.21 | 86.47 | 11.30 | 2.02 | 0.0 | 4.1 |
| 6NNU-3-300 | 0.16 | 86.36 | 11.52 | 1.96 | 0.0 | 4.6 |
| 6NNU-4-325 | 0.18 | 86.44 | 11.38 | 2.00 | 0.0 | 3.6 |
| 6NNU-5-350 | 0.20 | 87.45 | 11.41 | 0.94 | 0.0 | 2.6 |
| 6NNU-6-375 | 0.16 | 86.60 | 11.58 | 1.66 | 0.0 | 2.0 |
| 6NNU-7-400 | 0.16 | 86.18 | 11.28 | 2.38 | 0.0 | 0.5 |

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*The 5HCU-5-300 sample was broken after the metal analysis.
** +/- indicates the variations from three determinations.

TABLE VI (Continued)

| | Wt % | | | | ug/ml | |
|---|---|---|---|---|---|---|
| Sample | N | C | H | O by difference | Ti | Fe |
| 7NCU-1-300(12) | 0.14 | 86.63 | 11.41 | 1.82 | 0.0 | 0.0 |
| 7NCU-2-300(24) | 0.18 | 87.04 | 11.50 | 1.28 | 0.0 | 0.0 |
| 7NCU-3-300(32) | 0.12 | 87.24 | 11.59 | 1.05 | 0.0 | 0.0 |
| 7NCU-4-300(36) | 0.15 | 86.94 | 11.45 | 1.46 | 0.0 | 0.0 |
| 7NCU-5-300 | 0.13 | 87.25 | 11.46 | 1.16 | 0.0 | 0.0 |
| 7NCU-6-325 | 0.15 | 87.24 | 11.52 | 1.09 | 0.0 | 0.0 |
| 7NCU-7-350 | 0.17 | 87.44 | 11.34 | 1.05 | 0.0 | 0.0 |
| 7NCU-8-375 | 0.15 | 87.49 | 11.21 | 1.15 | 0.0 | 0.0 |
| 8HCU-1-300(12) | 0.12 | 86.99 | 11.76 | 1.13 | 0.0 | 0.0 |
| 8HCU-2-300(24) | 0.14 | 87.13 | 11.44 | 1.29 | 0.0 | 0.0 |
| 8HCU-3-300(32) | 0.11 | 87.47 | 11.49 | 0.93 | 0.0 | 0.0 |
| 8HCU-4-300(36) | 0.16 | 87.92 | 11.69 | 0.23 | 0.0 | 0.0 |
| 8HCU-5-300 | 0.12 | 87.13 | 11.72 | 1.03 | 0.0 | 0.0 |
| 8HCU-6-325 | 0.14 | 87.18 | 11.76 | 0.92 | 0.0 | 0.0 |
| * +/- | 0.01 | 0.35 | 0.19 | 0.16 | | |
| 8HCU-7-350 | 0.12 | 87.31 | 11.96 | 0.61 | 0.0 | 0.0 |
| * +/- | 0.03 | 0.04 | 0.14 | 0.11 | | |
| 8HCU-8-375 | 0.11 | 87.47 | 12.13 | 0.30 | 0.0 | 0.0 |
| * +/- | 0.01 | 0.20 | 0.16 | 0.34 | | |

---

* +/- indicates the variations from three determinations.

TABLE VI (Continued)

| Sample | Wt % N | Wt % C | Wt % H | Wt % O by difference | ug/ml Ti | ug/ml Fe |
|---|---|---|---|---|---|---|
| 9NCD-1-300(12) | 0.12 | 86.63 | 11.43 | 1.80 | 8.0 | 0.0 |
| 9NCD-2-300(24) | 0.12 | 86.83 | 11.52 | 1.47 | 12.0 | 0.0 |
| 9NCD-3-300(32) | 0.12 | 87.39 | 11.67 | 0.82 | 19.0 | 0.0 |
| 9NCD-4-300(36) | 0.11 | 87.40 | 11.66 | 0.79 | 11.0 | 0.0 |
| 9NCD-5-300 | 0.20 | 88.21 | 11.52 | 0.07 | 16.0 | 0.0 |
| 9NCD-6-325 | 0.15 | 87.94 | 11.54 | 0.37 | 9.0 | 0.0 |
| 9NCD-7-350 | 0.17 | 87.89 | 11.45 | 0.49 | 2.0 | 0.0 |
| 9NCD-8-375 | 0.13 | 87.05 | 11.31 | 0.51 | 0.0 | 0.0 |
| 10HCD-1-300(12) | 0.11 | 87.28 | 11.79 | 0.82 | 3.0 | 0.0 |
| 10HCD-2-300(24) | 0.15 | 87.43 | 11.79 | 0.63 | 5.0 | 0.0 |
| 10HCD-3-300(32) | 0.13 | 87.43 | 11.76 | 0.68 | 10.0 | 0.0 |
| 10HCD-4-300(36) | 0.13 | 87.47 | 11.75 | 0.65 | 12.0 | 0.0 |
| 10HCD-5-300 | 0.13 | 87.31 | 11.70 | 0.86 | 8.0 | 0.0 |
| 10HCD-6-325 | 0.13 | 87.16 | 11.83 | 0.88 | 0.0 | 0.0 |
| * +/- | 0.02 | 0.17 | 0.01 | 0.19 | | |
| 10HCD-7-350 | 0.10 | 87.28 | 11.99 | 0.61 | 0.0 | 0.0 |
| * +/- | 0.03 | 0.16 | 0.14 | 0.36 | | |
| 10HCD-8-375 | 0.08 | 87.43 | 11.91 | 0.57 | 0.0 | 0.0 |
| * +/- | 0.005 | 0.30 | 0.22 | 0.52 | | |

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* +/- indicates the variations from three determinations.

TABLE VI (Continued)

| | Wt % | | | | ug/ml | |
|---|---|---|---|---|---|---|
| Sample | N | C | H | O by difference | Ti | Fe |
| 11HND-1-250 | 0.18 | 86.61 | 11.65 | 1.56 | 20.0 | 14.4 |
| 11HND-2-275 | 0.16 | 86.44 | 11.35 | 2.05 | 27.0 | 13.8 |
| 11HND-3-300 | 0.18 | 86.44 | 11.31 | 2.07 | 30.0 | 15.2 |
| 11HND-4-325 | 0.18 | 86.69 | 11.39 | 1.74 | 31.0 | 6.7 |
| 11HND-5-350 | 0.21 | 86.71 | 11.33 | 1.75 | 34.0 | 4.4 |
| 11HND-6-375 | 0.18 | 86.14 | 11.34 | 2.34 | 20.0 | 2.4 |
| 11HND-7-400 | 0.13 | 87.11 | 11.51 | 1.25 | 9.0 | 2.7 |
| 12NND-1-250 | 0.18 | 86.51 | 11.16 | 2.15 | 18.0 | 4.7 |
| 12NND-2-275 | 0.18 | 86.46 | 11.49 | 1.87 | 25.0 | 13.6 |
| 12NND-3-300 | 0.19 | 86.24 | 11.29 | 2.28 | 28.0 | 15.2 |
| 12NND-4-325 | 0.19 | 86.45 | 11.49 | 1.87 | 31.0 | 17.0 |
| 12NND-5-350 | 0.18 | 86.37 | 11.18 | 2.27 | 28.0 | 16.4 |
| 12NND-6-375 | 0.19 | 86.64 | 11.38 | 1.79 | 25.0 | 15.2 |
| 12NND-7-400 | 0.13 | 86.38 | 11.51 | 1.98 | 19.0 | 6.7 |

# APPENDIX C

# RESULTS OF SIMULATED DISTILLATION

## RESULTS OF SIMULATED DISTILLATION

The simulated distillation analysis was performed by using a Hewlett Packard Model 5880A Gas Chromatograph equipped with a packed column. The detector used was a thermal conductivity type. The operating oven condition was set from the initial temperature of 40 C to the final temperature of 320 C with a heating rate of 7 C per minute. A mixture of normal paraffins including hexane, heptane, octane, decane, pentadecane, and hexadecane was used as a calibration standard for the correlation of the retention time and boiling temperature. A sample size of 0.8 ul was employed for the analysis.

The method of calculation for the boiling distribution range was adopted from the ASTM D-2887 technique. The result of the retention time and peak area of each sample was converted to the temperature and cumulative area relation by using the retention and temperature correlation obtained from the result of the calibration standard. From the tabulated results of temperature versus cumulative area, the intial boiling point is defined as the temperature which corresponds to the cumulative area of 0.5 %, while the end point is the temperature at the cumulative area of 99.5 %. Between the interval of initial boiling point and end point, the boiling temperatures were reported at each 10 % cumulative area. Linear interpolation was used to determine the boiling temperature associated with every 10 % cumulative area.

The results of the boiling range of samples obtained from different runs along with those of the feed are given in Table VII through Table XVI. A few duplicated measurements showed a maximum variation of retention time of 0.03 min.

# TABLE VII

# SIMULATED DISTILLATION FOR SAMPLES TREATED UNDER NITROGEN/NON-CATALYTIC CONDITION OF THE UNDOCTORED FEEDSTOCK (2NNU)

| Area % * | Temperature (C) | | | | |
|---|---|---|---|---|---|
| | Feed | 1-250** | 2-275 | 3-300 | 4-325 |
| IBP | 160 | 114 | 113 | 115 | 113 |
| 10 | 214 | 114 | 113 | 115 | 113 |
| 20 | 237 | 114 | 183 | 144 | 189 |
| 30 | 256 | 118 | 225 | 220 | 229 |
| 40 | 271 | 218 | 251 | 246 | 255 |
| 50 | 288 | 248 | 271 | 269 | 275 |
| 60 | 303 | 273 | 292 | 291 | 297 |
| 70 | 315 | 298 | 310 | 310 | 315 |
| 80 | 338 | 324 | 337 | 338 | 340 |
| 90 | 368 | 364 | 372 | 374 | 385 |
| EBP | 436 | 463 | 451 | 460 | 469 |

* Chromatographic area % : Since the response factor for most hydrocarbon is about unity, the area percent closely approximates the weight percent.

** Sample names are coded to include three groups of

TABLE VII (Continued)

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(Footnote continued)

numbers. The first number is designated for the consecutive sample number. The second group is designated for the temperature when the sample was taken. The third number in parenthesis is designated for the period in hour when the sample was taken during the catalyst stabilization period in the catalytic runs.

## TABLE VII (Continued)

| Area % | Temperature (C) | | |
|---|---|---|---|
| | Feed | 5-350 | 6-375 |
| IBP | 160 | 112 | 111 |
| 10 | 214 | 112 | 111 |
| 20 | 237 | 206 | 207 |
| 30 | 256 | 239 | 239 |
| 40 | 271 | 261 | 260 |
| 50 | 288 | 279 | 278 |
| 60 | 303 | 301 | 298 |
| 70 | 315 | 322 | 313 |
| 80 | 338 | 342 | 340 |
| 90 | 368 | 386 | 379 |
| EBP | 436 | 470 | 469 |

## TABLE VIII

## SIMULATED DISTILLATION FOR SAMPLES TREATED UNDER HYDROGEN/NON-CATALYTIC CONDITION OF THE UNDOCTORED FEEDSTOCK (3HNU)

| Area % | Temperature (C) | | | | |
|---|---|---|---|---|---|
| | Feed | 1-250 | 2-275 | 3-300 | 4-325 |
| IBP | 160 | 110 | 109 | 109 | 108 |
| 10 | 214 | 110 | 173 | 170 | 189 |
| 20 | 237 | 211 | 220 | 218 | 225 |
| 30 | 256 | 237 | 243 | 241 | 247 |
| 40 | 271 | 255 | 262 | 260 | 266 |
| 50 | 288 | 272 | 278 | 276 | 283 |
| 60 | 303 | 292 | 296 | 294 | 301 |
| 70 | 315 | 306 | 312 | 309 | 320 |
| 80 | 338 | 331 | 334 | 332 | 345 |
| 90 | 368 | 362 | 368 | 364 | 379 |
| EBP | 436 | 438 | 439 | 437 | 456 |

TABLE VIII (Continued)

| Area % | Temperature (C) | | | |
|---|---|---|---|---|
| | Feed | 5-350 | 6-375 | 7-400 |
| IBP | 160 | 108 | 108 | 108 |
| 10 | 214 | 188 | 192 | 190 |
| 20 | 237 | 224 | 226 | 224 |
| 30 | 256 | 245 | 247 | 246 |
| 40 | 271 | 263 | 266 | 264 |
| 50 | 288 | 279 | 282 | 280 |
| 60 | 303 | 297 | 300 | 299 |
| 70 | 315 | 313 | 319 | 312 |
| 80 | 338 | 334 | 335 | 336 |
| 90 | 368 | 366 | 375 | 378 |
| EBP | 436 | 437 | 439 | 458 |

## TABLE IX

## SIMULATED DISTILLATION FOR SAMPLES TREATED UNDER HYDROGEN/CATALYTIC CONDITION OF THE UNDOCTORED FEEDSTOCK (5HCU)

| Area % | Temperature (C) | | | | |
|---|---|---|---|---|---|
| | Feed | 1-300(12) | 2-300(24) | 3-300(32) | 4-300(36) |
| IBP | 160 | 58 | 94 | 103 | 109 |
| 10 | 214 | 203 | 201 | 212 | 209 |
| 20 | 237 | 231 | 228 | 236 | 231 |
| 30 | 256 | 251 | 248 | 251 | 251 |
| 40 | 271 | 268 | 266 | 270 | 268 |
| 50 | 288 | 284 | 282 | 286 | 285 |
| 60 | 303 | 302 | 299 | 302 | 301 |
| 70 | 315 | 319 | 312 | 318 | 316 |
| 80 | 338 | 340 | 336 | 337 | 339 |
| 90 | 368 | 373 | 365 | 369 | 368 |
| EBP | 436 | 436 | 436 | 434 | 437 |

TABLE IX (Continued)

| Area % | Temperature (C) | | | | |
|---|---|---|---|---|---|
| | Feed | 5-300 | 6-325 | 7-350 | 8-375 |
| IBP | 160 | 115 | 120 | 100 | 98 |
| 10 | 214 | 209 | 208 | 204 | 204 |
| 20 | 237 | 231 | 233 | 232 | 232 |
| 30 | 256 | 251 | 251 | 252 | 252 |
| 40 | 271 | 268 | 269 | 269 | 269 |
| 50 | 288 | 285 | 287 | 285 | 285 |
| 60 | 303 | 301 | 302 | 302 | 302 |
| 70 | 315 | 316 | 319 | 313 | 319 |
| 80 | 338 | 339 | 344 | 337 | 337 |
| 90 | 368 | 368 | 369 | 367 | 378 |
| EBP | 436 | 436 | 430 | 442 | 443 |

# TABLE X

# SIMULATED DISTILLATION FOR SAMPLES TREATED UNDER NITROGEN/NON-CATALYTIC CONDITION OF THE UNDOCTORED FEEDSTOCK (6NNU)

| Area % | Temperature (C) | | | | |
|---|---|---|---|---|---|
| | Feed | 1-250 | 2-275 | 3-300 | 4-325 |
| IBP | 160 | 98 | 100 | 100 | 132 |
| 10 | 214 | 205 | 209 | 208 | 212 |
| 20 | 237 | 234 | 237 | 235 | 236 |
| 30 | 256 | 254 | 256 | 251 | 256 |
| 40 | 271 | 270 | 271 | 270 | 272 |
| 50 | 288 | 287 | 288 | 287 | 292 |
| 60 | 303 | 303 | 304 | 303 | 306 |
| 70 | 315 | 315 | 316 | 315 | 324 |
| 80 | 338 | 337 | 338 | 337 | 348 |
| 90 | 368 | 373 | 374 | 376 | 385 |
| EBP | 436 | 441 | 442 | 452 | 475 |

TABLE X (Continued)

| Area % | Temperature (C) | | | |
|---|---|---|---|---|
| | Feed | 5-350 | 6-375 | 7-400 |
| IBP | 160 | 153 | 131 | 153 |
| 10 | 214 | 216 | 213 | 213 |
| 20 | 237 | 241 | 238 | 233 |
| 30 | 256 | 259 | 254 | 253 |
| 40 | 271 | 274 | 272 | 271 |
| 50 | 288 | 293 | 289 | 287 |
| 60 | 303 | 306 | 305 | 303 |
| 70 | 315 | 323 | 321 | 321 |
| 80 | 338 | 350 | 347 | 346 |
| 90 | 368 | 380 | 374 | 377 |
| EBP | 436 | 442 | 437 | 477 |

# TABLE XI

## SIMULATED DISTILLATION FOR SAMPLES TREATED UNDER NITROGEN/CATALYTIC CONDITION OF THE UNDOCTORED FEEDSTOCK (7NCU)

| Area % | Temperature (C) | | | | |
|---|---|---|---|---|---|
| | Feed | 1-300(12) | 2-300(24) | 3-300(32) | 4-300(36) |
| IBP | 160 | 152 | 153 | 153 | 153 |
| 10 | 214 | 214 | 214 | 213 | 215 |
| 20 | 237 | 237 | 238 | 239 | 239 |
| 30 | 256 | 257 | 256 | 256 | 256 |
| 40 | 271 | 274 | 274 | 273 | 273 |
| 50 | 288 | 291 | 290 | 290 | 289 |
| 60 | 303 | 305 | 306 | 306 | 305 |
| 70 | 315 | 323 | 322 | 323 | 318 |
| 80 | 338 | 345 | 347 | 348 | 338 |
| 90 | 368 | 378 | 376 | 379 | 372 |
| EBP | 436 | 439 | 438 | 436 | 439 |

TABLE XI (Continued)

| Area % | Temperature (C) | | | | |
|---|---|---|---|---|---|
| | Feed | 5-300 | 6-325 | 7-350 | 8-375 |
| IBP | 160 | 159 | 162 | 162 | 157 |
| 10 | 214 | 215 | 218 | 218 | 215 |
| 20 | 237 | 241 | 242 | 242 | 239 |
| 30 | 256 | 257 | 257 | 257 | 259 |
| 40 | 271 | 274 | 274 | 274 | 274 |
| 50 | 288 | 291 | 292 | 293 | 293 |
| 60 | 303 | 307 | 306 | 308 | 307 |
| 70 | 315 | 323 | 320 | 324 | 328 |
| 80 | 338 | 344 | 342 | 346 | 347 |
| 90 | 368 | 376 | 370 | 378 | 378 |
| EBP | 436 | 439 | 429 | 440 | 439 |

# TABLE XII

# SIMULATED DISTILLATION FOR SAMPLES TREATED UNDER HYDROGEN/CATALYTIC CONDITION OF THE UNDOCTORED FEEDSTOCK (8HCU)

| Area % | Temperature (C) | | | | |
|---|---|---|---|---|---|
| | Feed | 1-300(12) | 2-300(24) | 3-300(32) | 4-300(36) |
| IBP | 160 | 123 | 143 | 136 | 142 |
| 10 | 214 | 206 | 210 | 208 | 209 |
| 20 | 237 | 234 | 238 | 235 | 236 |
| 30 | 256 | 253 | 255 | 253 | 255 |
| 40 | 271 | 269 | 272 | 270 | 270 |
| 50 | 288 | 285 | 289 | 288 | 288 |
| 60 | 303 | 302 | 305 | 303 | 305 |
| 70 | 315 | 314 | 318 | 315 | 317 |
| 80 | 338 | 337 | 341 | 337 | 340 |
| 90 | 368 | 371 | 379 | 372 | 373 |
| EBP | 436 | 441 | 443 | 441 | 442 |

## TABLE XII (Continued)

| Area % | Temperature (C) | | | | |
|---|---|---|---|---|---|
| | Feed | 5-300 | 6-325 | 7-350 | 8-375 |
| IBP | 160 | 144 | 142 | 147 | 146 |
| 10 | 214 | 212 | 213 | 213 | 210 |
| 20 | 237 | 238 | 239 | 236 | 234 |
| 30 | 256 | 254 | 253 | 255 | 253 |
| 40 | 271 | 272 | 271 | 271 | 269 |
| 50 | 288 | 289 | 288 | 288 | 287 |
| 60 | 303 | 305 | 304 | 303 | 302 |
| 70 | 315 | 319 | 320 | 316 | 315 |
| 80 | 338 | 341 | 340 | 341 | 338 |
| 90 | 368 | 374 | 373 | 368 | 372 |
| EBP | 436 | 440 | 435 | 434 | 434 |

# TABLE XIII

# SIMULATED DISTILLATION FOR SAMPLES TREATED UNDER NITROGEN/CATALYTIC CONDITION OF THE DOCTORED FEEDSTOCK (9NCD)

| Area % | Temperature (C) | | | | |
|---|---|---|---|---|---|
| | Feed | 1-300(12) | 2-300(24) | 3-300(32) | 4-300(36) |
| IBP | 160 | 152 | 153 | 155 | 155 |
| 10 | 214 | 215 | 215 | 215 | 215 |
| 20 | 237 | 239 | 239 | 240 | 240 |
| 30 | 256 | 258 | 256 | 255 | 256 |
| 40 | 271 | 274 | 274 | 273 | 273 |
| 50 | 288 | 291 | 291 | 290 | 291 |
| 60 | 303 | 307 | 306 | 305 | 306 |
| 70 | 315 | 323 | 322 | 321 | 322 |
| 80 | 338 | 346 | 348 | 342 | 345 |
| 90 | 368 | 380 | 375 | 371 | 374 |
| EBP | 436 | 440 | 437 | 435 | 436 |

TABLE XIII (Continued)

| Area % | Temperature (C) | | | | |
|---|---|---|---|---|---|
| | Feed | 5-300 | 6-325 | 7-350 | 8-375 |
| IBP | 160 | 160 | 160 | 151 | 153 |
| 10 | 214 | 216 | 215 | 213 | 214 |
| 20 | 237 | 242 | 241 | 238 | 240 |
| 30 | 256 | 258 | 257 | 254 | 255 |
| 40 | 271 | 274 | 274 | 272 | 273 |
| 50 | 288 | 291 | 291 | 289 | 293 |
| 60 | 303 | 307 | 307 | 305 | 306 |
| 70 | 315 | 323 | 323 | 318 | 325 |
| 80 | 338 | 345 | 345 | 342 | 344 |
| 90 | 368 | 375 | 376 | 376 | 375 |
| EBP | 436 | 438 | 439 | 458 | 455 |

# TABLE XIV

# SIMULATED DISTILLATION FOR SAMPLES TREATED UNDER HYDROGEN/CATALYTIC CONDITION OF THE DOCTORED FEEDSTOCK (10HCD)

| Area % | Temperature (C) | | | | |
|---|---|---|---|---|---|
| | Feed | 1-300(12) | 2-300(24) | 3-300(32) | 4-300(36) |
| IBP | 160 | 144 | 140 | 155 | 145 |
| 10 | 214 | 212 | 211 | 214 | 213 |
| 20 | 237 | 236 | 235 | 239 | 237 |
| 30 | 256 | 254 | 253 | 256 | 252 |
| 40 | 271 | 270 | 270 | 272 | 271 |
| 50 | 288 | 287 | 286 | 289 | 287 |
| 60 | 303 | 303 | 303 | 305 | 304 |
| 70 | 315 | 319 | 319 | 321 | 320 |
| 80 | 338 | 338 | 339 | 346 | 342 |
| 90 | 368 | 370 | 372 | 375 | 369 |
| EBP | 436 | 436 | 435 | 436 | 435 |

TABLE XIV (Continued)

| Area % | Temperature (C) | | | | |
|---|---|---|---|---|---|
| | Feed | 5-300 | 6-325 | 7-350 | 8-375 |
| IBP | 160 | 153 | 155 | 136 | 140 |
| 10 | 214 | 214 | 219 | 211 | 213 |
| 20 | 237 | 239 | 242 | 236 | 238 |
| 30 | 256 | 256 | 256 | 253 | 254 |
| 40 | 271 | 273 | 272 | 271 | 271 |
| 50 | 288 | 290 | 288 | 288 | 288 |
| 60 | 303 | 306 | 302 | 304 | 304 |
| 70 | 315 | 322 | 318 | 321 | 321 |
| 80 | 338 | 337 | 336 | 335 | 339 |
| 90 | 368 | 374 | 360 | 372 | 368 |
| EBP | 436 | 436 | 426 | 439 | 434 |

# TABLE XV

# SIMULATED DISTILLATION FOR SAMPLES TREATED UNDER HYDROGEN/NON-CATALYTIC CONDITION OF THE DOCTORED FEEDSTOCK (11HND)

| Area % | Temperature (C) | | | | |
|---|---|---|---|---|---|
| | Feed | 1-250 | 2-275 | 3-300 | 4-325 |
| IBP | 160 | 157 | 167 | 161 | 157 |
| 10 | 214 | 214 | 218 | 215 | 214 |
| 20 | 237 | 239 | 242 | 241 | 238 |
| 30 | 256 | 255 | 260 | 256 | 254 |
| 40 | 271 | 272 | 275 | 272 | 271 |
| 50 | 288 | 290 | 293 | 289 | 287 |
| 60 | 303 | 306 | 307 | 303 | 303 |
| 70 | 315 | 322 | 323 | 317 | 319 |
| 80 | 338 | 347 | 345 | 340 | 338 |
| 90 | 368 | 375 | 380 | 373 | 367 |
| EBP | 436 | 429 | 442 | 442 | 434 |

## TABLE XV (Continued)

| Area % | Temperature (C) | | | |
|---|---|---|---|---|
| | Feed | 5-350 | 6-375 | 7-400 |
| IBP | 160 | 151 | 151 | 160 |
| 10 | 214 | 213 | 213 | 216 |
| 20 | 237 | 238 | 238 | 242 |
| 30 | 256 | 254 | 253 | 257 |
| 40 | 271 | 271 | 271 | 273 |
| 50 | 288 | 288 | 287 | 291 |
| 60 | 303 | 304 | 303 | 307 |
| 70 | 315 | 321 | 320 | 323 |
| 80 | 338 | 338 | 335 | 343 |
| 90 | 368 | 373 | 369 | 375 |
| EBP | 436 | 459 | 459 | 438 |

## TABLE XVI

## SIMULATED DISTILLATION FOR SAMPLES TREATED UNDER NITROGEN/NON-CATALYTIC CONDITION OF THE DOCTORED FEEDSTOCK (12NND)

| Area % | Temperature (C) | | | | |
|---|---|---|---|---|---|
| | Feed | 1-250 | 2-275 | 3-300 | 4-325 |
| IBP | 160 | 144 | 163 | 161 | 160 |
| 10 | 214 | 214 | 215 | 217 | 205 |
| 20 | 237 | 240 | 241 | 242 | 239 |
| 30 | 256 | 256 | 257 | 257 | 254 |
| 40 | 271 | 274 | 272 | 274 | 272 |
| 50 | 288 | 290 | 290 | 294 | 290 |
| 60 | 303 | 307 | 304 | 307 | 305 |
| 70 | 315 | 322 | 326 | 324 | 322 |
| 80 | 338 | 344 | 347 | 345 | 343 |
| 90 | 368 | 374 | 382 | 379 | 375 |
| EBP | 436 | 436 | 442 | 441 | 430 |

TABLE XVI (Continued)

| Area % | Temperature (C) | | | |
|---|---|---|---|---|
| | Feed | 5-350 | 6-375 | 7-400 |
| IBP | 160 | 164 | 161 | 152 |
| 10 | 214 | 216 | 215 | 215 |
| 20 | 237 | 241 | 239 | 241 |
| 30 | 256 | 258 | 254 | 257 |
| 40 | 271 | 272 | 271 | 274 |
| 50 | 288 | 290 | 287 | 291 |
| 60 | 303 | 305 | 302 | 307 |
| 70 | 315 | 318 | 322 | 322 |
| 80 | 338 | 340 | 341 | 343 |
| 90 | 368 | 373 | 375 | 375 |
| EBP | 436 | 427 | 429 | 438 |

# VITA 2

Wichai Mahorankit

Candidate for the Degree of

Master of Science

Thesis: EFFECTS OF TITANOCENE DICHLORIDE ON FREE RADICAL FORMATION DURING TREATMENT OF A COAL-DERIVED LIQUID

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Bangkok, Thailand, December 28, 1962, the son of Chalin and Jintana.

Education: Received Bachelor of Engineering degree in Chemical Engineering from Chulalongkorn University in 1984; completed requirements for the Master of Science degree at Oklahoma State University in May 1988.

Professional Experience: Engineering Trainee in Asahi (Bangkok) co., ltd, in 1983; Process Engineer in Khoa Chong (Coffee) Industry in 1984.