

HYDROUS METAL OXIDE ION EXCHANGERS AS
HYDROGENATION CATALYSTS FOR DIRECT COAL LIQUEFACTION*

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INTRODUCTION

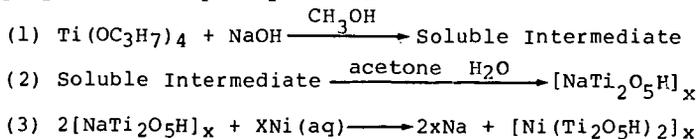
Interest in efficient conversion of coal to liquid fuels has encouraged exploration of promising catalytic systems for direct coal liquefaction. We have identified a group of hydrous oxide ion exchange compounds of Ti, Zr, Nb, and Ta which can be used to prepare hydrogenation catalysts by a novel synthesis route involving exchange of active metals into these compounds. Hydrous oxide ion exchange compounds have previously been investigated at Sandia National Laboratories for use in decontamination of aqueous nuclear waste (1,2) and as precursors for ceramic materials (3). A number of properties of the compounds suggested their use as substrates for catalyst preparation: 1) any metal or mixture of metals can be atomically dispersed in the materials over a wide concentration range by a simple process; 2) the materials have high surface areas; 3) they exhibit good chemical stability; 4) solution chemistry or high temperature reactions can be used to provide active metal oxidation state control; and 5) acidity and basicity of the substrate can be modified by ion exchange.

Although these properties suggested hydrous oxide ion exchangers may exhibit wide versatility for catalyst preparation, it was not known if catalysts synthesized by exchanging ions of active metals into the material would exhibit hydrogenation activity. The purpose of the experiments reported here was to explore the hydrogenation activity of these materials for slurry phase catalysis of direct coal liquefaction. It is also possible that hydrous metal oxide ion exchangers may be used to prepare multifunctional catalysts and catalysts for other reactions such as oxidation or dehydrogenation.

EXPERIMENTAL

Preparation and Characterization of Catalysts

The titanate system, the best characterized and least expensive of the hydrous oxides, was chosen for exploratory testing. Titanate catalysts were prepared by exchanging the sodium ions of a hydrous oxide titanium compound, generically called sodium titanate (ST), with the desired metal ions in aqueous solution. ST was prepared by reacting tetraisopropyl titanate with sodium hydroxide in methanol, hydrolyzing the solution in a water acetone mixture and drying the resulting precipitate at ambient temperature under vacuum. The preparation steps may be illustrated as follows:



* This work supported by the U. S. Dept. of Energy, Contract No. DE-AC04-76DP00789.

A typical ST product is an amorphous fluffy powder, which contains approximately 20% residual volatile constituents, predominately water and minor amounts of alcohols. The titanates of other metals, formed by exchange of the sodium ions, were found to have the same morphology and volatile content as the starting ST material. Drying the titanates at elevated temperature resulted in loss of volatiles. Approximately 90% of the volatiles were removed at 200°C and greater than 95% were removed after heating to 400°C. X-ray diffraction and SEM work indicated that a transition from an amorphous to a crystalline form (rutile) occurs at approximately 600°C. This is supported by DTA and TGA studies, which showed a large exotherm with no corresponding weight change at the same temperature.

Surface areas and pore volumes for several titanates have been measured by nitrogen BET and adsorption-desorption techniques. Surface areas for the material ranged from 150 to 300 m²/g and the desorption pore volumes from 0.24 to 0.41 cc/g. All of the titanates had bimodal pore volume distributions similar to the distribution illustrated for Ni titanate (total pore volume = 0.31) in Figure 1. For comparison, the unimodal pore volume distribution for a Ni/Mo on alumina catalyst, Shell 324, (total pore volume = 0.44) is also shown.

Materials, Apparatus and Procedure

Liquefaction reactions were performed with Illinois No. 6 (Burning Star) coal, SRC-II heavy distillate solvent from the Ft. Lewis Pilot Plant (1:2 coal:solvent, by weight) and high purity hydrogen. Shell 324, a 2.7% Ni/13.2% Mo on alumina catalyst, currently used in integrated two stage liquefaction pilot plant studies (4), was ground to -200 mesh and used as a reference for comparison of catalytic activity. Control experiments were also performed without catalyst addition.

As a result of screening liquefaction experiments with a number of titanates, including Cr⁺³, Fe⁺³, Fe⁺², Ni⁺², Pd⁺², Mo*, Rh⁺³, Ru⁺³, Co⁺², Mn⁺² and Eu⁺³, three were chosen to test the effects of active metal, metal loading and post-preparation treatment on catalytic activity.

A randomized factorial experimental plan (3 x 2 with duplication) was used to test the effect of active metal and metal loading on liquefaction activity. For these experiments, Ni, Mo and Pd titanates with metal loadings of 1% and 10%, by weight of titanate, were used. Catalyst weight added to the reactor was adjusted so that liquefaction reactions with the 1% titanates were performed with 4 x 10⁻⁵ moles of active metal and reactions with the 10% titanates with 4 x 10⁻⁴ moles. To test the effects of catalyst post-preparation treatments, which result in loss of volatiles and surface area, and oxidation or reduction of the Ni, duplicate experiments were performed with the 10% Ni titanate heated for two hours at six conditions--300, 450 and 700°C in air and hydrogen. Reference experiments with Shell 324 were performed with the same number of moles of active metal (Ni + Mo) as the 10% loading experiments.

All liquefaction reactions were performed in 40 cm³ microreactors which were charged with 2.67 g of coal, 5.33 g SRC-II,

* Oxidation state not determined.

and powdered catalyst, pressurized to 800 psig (cold) with hydrogen, then heated to 425°C for 30 minutes and shaken at ~150 cycles/min. during the heating period. Temperatures and pressures were accurately recorded with a digital data acquisition system during the course of the experiments. Following the heating period of each experiment, the reaction vessel was quenched to ambient temperature, the resulting pressure was recorded, a gas sample was taken, and the product slurry was subsampled for analysis.

Product Analyses

Gas samples were analyzed for mole percentages of CO, CO₂, H₂S and C₁-C₄ hydrocarbons with a Hewlett-Packard 5710A gas chromatograph, which was calibrated with standard mixtures (Matheson Gas Products) of hydrocarbon gases in hydrogen. Hydrogen in the samples was obtained by difference as the remainder of the product gas mixture. The quantity of each gas produced was calculated from the mole percent in the gas sample and the post-reaction vessel temperature and pressure using an ideal gas law calculation. Hydrogen consumed during the reaction, obtained as the difference between the initial charge and hydrogen remaining after the reactor was quenched, was reported on a percent dmmf coal basis.

The reaction product slurry was analyzed for insols, high molecular weight (mw) product, intermediate mw product and low mw product by tetrahydrofuran (THF) solubility and high performance liquid chromatography (HPLC). A 0.2 g subsample was mixed with about 50 ml of THF, filtered to obtain the weight of insols, and brought to 100 ml with additional THF. Chromatograms of 5 μ l aliquots of the filtrate were obtained with a Waters Assoc. Model 6000A solvent delivery system, a 100 Å microstyragel gel permeation column, and a Model 440 uv absorbance detector. The uv absorbance response factors for the product groups were determined using calibration samples prepared by dissolving known weights of high (~1000 g/mole), intermediate (~500 g/mole) and low (250 g/mole) mw coal-derived products obtained by preparative scale liquid chromatographic (gel permeation) separation of whole liquid product from liquefaction reactions performed under similar conditions with the same coal and solvent. Chromatogram area measurements and response factors were used to calculate the percentages of high, intermediate and low* mw products for the THF soluble product. Conversion data were calculated on a dmmf coal basis, and included corrections for the conversion of the pyrite content of the coal to pyrrhotite and the loss of volatiles, if any, from the catalyst.

RESULTS AND DISCUSSION

Previous statistical analysis of experiments with oil soluble catalysts (5) has shown that hydrogen consumption and conversion to low mw product may be used as quantitative measures of catalyst activity for coal liquefaction. Figures 2 and 3 illustrate the conversion to low mw product and hydrogen consumption for the experiment with the 1 and 10% Ni, Mo and Pd titanates without post-preparation treatments. The values represented in the figures are the averages of duplicate experiments. Standard deviations were statistically determined to be 1.4% for conversion

* % conversion to low mw product is approximately equivalent to pentane soluble product.

to low mw product and 0.13% for hydrogen consumption. As can be seen from Figures 2 and 3, the ranking for metals effect with respect to both low mw conversion and hydrogen consumption is Pd > Mo > Ni and with respect to metals loading is 10% > 1%.

Results of a two way analysis of variance were used to make a quantitative comparison of performance. The effect of active metals (1 and 10% loadings averaged), were as follows:

low mw product:

Pd (47.7%) > Mo (45.3%) > Ni (43.0%) $F = 10.8, P < .01$;

hydrogen consumption:

Pd (1.86%) > Mo (1.65%) > Ni (1.35%) $F = 22.4, P < .005$,

where F is the variance ratio and P is the probability of a chance occurrence of the result. These values may be compared with the results of experiments without catalyst addition (low mw product = 26.8% and hydrogen consumption = 0.69%) and experiments with Shell 324 (low mw product = 42.8% and hydrogen consumption = 1.88%). It was found that the 10% titanates averaged 3.2% greater conversion ($F = 10.8, P < 0.01$) and 0.37% greater hydrogen consumption ($F = 35.0, P < .005$) than the 1% titanates.

Only one post-preparation treatment of the 10% Ni titanates was found to have a significant effect on catalytic activity. Experiments with the titanate heated to 700°C in air produced a conversion of 33.6% to low mw product and had a hydrogen consumption of 0.71% which was significantly lower than the values for the other treatments ($45.2 \pm 1\%$ and $1.5 \pm 0.2\%$). X-ray diffraction analysis of the post-preparation treated materials shows formation of NiTiO_3 for only the material heated to 700°C in air. The NiTiO_3 formed probably cannot be reduced to Ni under liquefaction conditions and therefore is not available for catalysis of hydrogenation reactions. This has been supported by preliminary oxygen chemisorption experiments which show that the 700°C/air treatment produces a catalyst that has less than half the active nickel of the other materials.

Although this preliminary study was brief in its scope, the results indicate that catalysts prepared using hydrous metal oxide exchange compounds show promise for potential application to coal liquefaction processes. The initial activities of the titanates appear to be at least comparable to a commercial catalyst currently used in pilot plant liquefaction studies. Considering the versatility of the hydrous oxide ion exchangers with respect to their potential for preparation of multi-metal loadings and adjustment of substrate acidity or basicity, it is possible that these materials can be used to produce improved catalysts for direct coal liquefaction and other hydrogenation processes.

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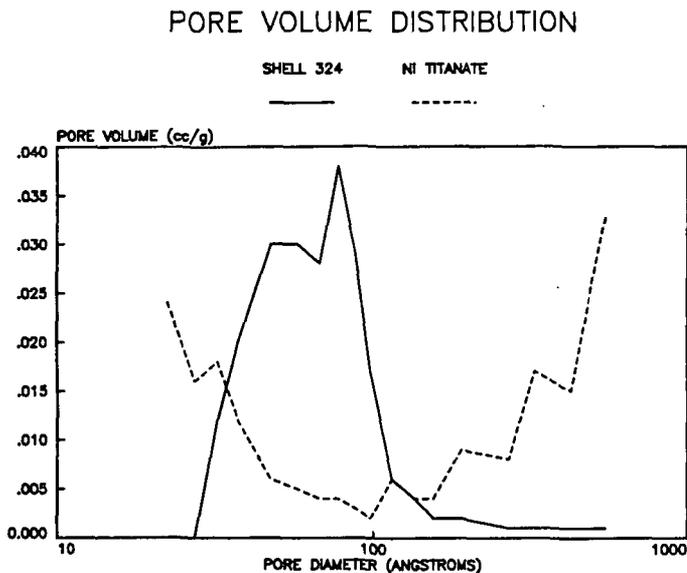


Figure 1

EFFECT OF ACTIVE METAL AND PERCENT LOADING ON CONVERSION TO LOW MW PRODUCT

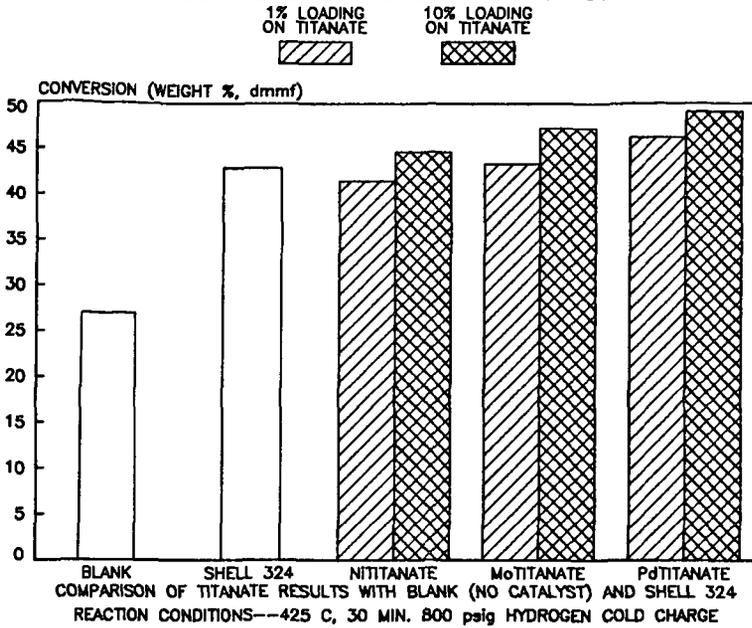


Figure 2

EFFECT OF ACTIVE METAL AND PERCENT LOADING ON HYDROGEN CONSUMPTION

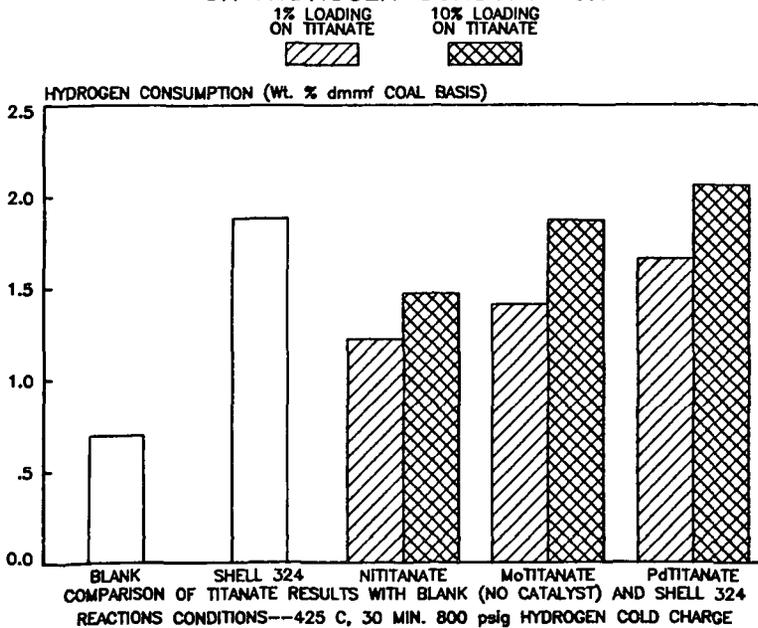


Figure 3

INTEGRATED TWO-STAGE LIQUEFACTION PROCESS - SOLVENT QUALITY EFFECTS

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Introduction

For the majority of the developed coal liquefaction processes the solvent is a portion of a selected liquefaction process stream, and not supplied from external sources, consequently a strict process control is needed to produce the required solvent balance and desired solvent quality.

Problems in maintaining both solvent balance and solvent quality has been particularly associated with the development of the SRC I process. With the introduction of the Two-Stage Liquefaction process in which SRC I is upgraded and converted to a distillate product the solvent balance does not constitute a problem anymore and the solvent quality has been improved.

Several modifications to the Two-Stage Liquefaction, which were dictated by important experimental results involving both the dissolution/hydrogenation of coal and the upgrading of the coal extract, led to a new process configuration in which first and second stages are interlocked in one integrated processing scheme. The major experimental results leading to these modifications are listed below:

- o Coal extract produced at lower operating severity than SRC I is more responsive to subsequent catalyzed reactions.^{1/}
- o Coal extracts produced at low severity can be upgraded to fuel products and a recycle process solvent of consistantly high quality.
- o Hydrogenated high boiling polyaromatics are superior hydrogen "donors" than compared to lower molecular weight tetralins.^{2/}
- o Nitrogen compounds inhibit catalytic hydrogenation of aromatics and deoxygenation of oxygen containing compounds in coal.^{3/}
- o Phenols inhibit catalytic denitrogenation of nitrogen compounds in coal or coal extracts.^{4/}
- o Heteroatom compounds, are not easily recovered since they form strong "adducts" with coals.
- o Hydrogenated polyaromatics, which also form "adducts" with coals are readily produced in the course of coal liquefaction/coal extract upgrading operations, providing a constant supply of steadily high quality recycle process solvent.

The first Integrated Two-Stage Liquefaction (ITSL) process configuration included Short Contact Time (SCT) coal extraction to maximize low severity operation in the first stage and LC-Fining using Shell 324 NiMo supported catalyst to provide extensive removal of heteroatom compounds. Further modifications of the ITSL process operating conditions were prompted by data obtained during actual

operation in the 3/4 ton coal/day ITSL process development unit at C-E Lummus, Engineering Development Center in New Brunswick, N.J., and by computed data and refining requirement as ascertained by upgrading coal-derived distillates from other processes. The major conclusions from all these sources can be summarized as follows:

- In a continuous operation the solvent fraction below 340-360°C is in vapor phase and participate little, if any, in the liquefaction of coal and also depresses the hydrogen partial pressure. Computed Vapor/Liquid equilibrium data confirm this fact.
- The -340°C fraction constitutes the most valuable refinery feedstock, being within the boiling range of gasoline, jet and diesel fuels.
- The +340°C fraction constitutes the best solvent quality for both dissolution of coal and hydrogen "shuttling."

The most recent ITSL process configuration, which is described below, attempts to exploit modifications indicated by these experimental results.

ITSL Process Flow Sheet

The current flow scheme of the ITSL operation is shown in Figure 1. Coal, hydrogen and recycle solvent (the +343°C fraction) react in the SCT reactor which is actually the SRC I preheater operated at higher outlet temperature (450°C). The gases and light oil are flashed off and the heavy oil (+343°C solvent/coal adduct) goes to the deasher. The deasher underflow containing virtually all of the ash and insoluble organic matter (IOM) goes to a vacuum flash, where the distillate portion goes overhead and combines with the deasher overflow. The ash/IOM containing flashed bottoms are drummed. Commercially this stream would go to a gasifier to generate the hydrogen for the process. The deasher overflow (cleaned +343°C solvent/coal adduct) combines with the vacuum flash overhead as feed to a continuous distillation column where the antisolvent is recovered overhead and the bottoms constitute the feed to the LC-Finer (LCFF) along with make-up hydrogen. The LC-Finer product (Total Liquid Product:TLP) is atmospherically flashed to collect the -343°C high quality product, and the +343°C bottoms are recycled to the SCT solvent pool. In this manner, the only product leaving the process is the -343°C fraction which has petroleum refinery feedstock quality superior to some petroleum crudes (Table 1).

Table 1
ITSL - PRODUCTS AND RECYCLE SOLVENT
Elemental Analysis

	<u>C</u>	<u>H</u>	<u>O</u>	<u>N</u>	<u>S</u>
Naphtha (C ₅ -177°C)	86	13	0.4	0.08	Traces
Fuel Oil (177-343°C)	88	11	0.3	0.08	0.01
Recycle Solvent (+343°C)	86	8	3.0	0.50	0.50

Phenols and nitrogen compounds are minor constituents of the process solvent compared to the level of polyaromatic hydrocarbons and they do not appear to

provide much contribution to the process solvent quality. Data examination of several ITSL recycle operations, as the coal-derived solvent replaces the hydrogenate creosote oil initial solvent, reveal the decrease of heteroatom compounds and at the same time the increase of the solvent quality. It is difficult to correlate these two experimental evidences since the more powerful the solvent becomes the more phenols and nitrogen compounds, present in the coal, are dissolved and in turn they can contribute to further the dissolution of the coal.

Bench-scale vacuum fractionation of the +343°C fraction of the recycle process solvent revealed that the heteroatom compounds, particularly nitrogen, are heavily concentrated in the +560°C distillation bottoms.

Boiling Point versus Solvent Quality (Conoco Inc.)

Relationship between boiling point and solvent quality was studied on a sample of ITSL recycle process solvent taken during steady state operation and in material balance. Twenty-two distillate fractions of ca. 100 ml. each were collected and analyzed by ¹H-NMR for proton distribution. Every third fraction was used for kinetic and equilibrium microautoclave tests.

Proton distribution of the distillate fractions are given in Table 2 along with the weight percent hydrogen for those fractions used in the microautoclave tests.

Table 2
Proton Distribution of Distillate Fractions

Fraction	Boiling Point °C	H ₂ Wt %	Condensed Aromatics	Cyclics α + β	Alkyls α + β	Alkyl γ
1	203	10.26	9.6	30.4	36.3	15.0
4	323	9.33	15.7	34.3	29.7	12.6
7	349	8.86	20.8	36.4	26.9	10.8
10	383	8.20	26.8	34.4	24.3	9.4
13	410	7.81	31.0	31.0	23.6	8.9
16	423	7.32	35.8	29.3	21.7	7.7
19	498	7.20	36.6	30.4	21.0	6.5
22	514	6.70	36.2	30.6	20.5	5.5

As the boiling point of the fractions increases the concentration of condensed aromatics increases from 8 to 39 percent. The results of the concentration of uncondensed aromatics are not shown since it decreases from 10 to 6 percent by the third fraction then remains fairly constant. The concentration of cyclic alpha and beta (naphthenic) protons, which provide one measure of donor concentration, increases for the first ten fractions, then decreases continuously to 31 percent. The concentration of alkyl alpha, beta and gamma protons which provide a measure of paraffins content decreases over the range with boiling point. Weight percent hydrogen decreases monotonically with increasing boiling point.

Microautoclave tests were carried out at 1000 psig (cold) nitrogen pressure, and are shown in Figure 2. At kinetic conditions, conversion increases sharply with boiling point to approximately 350°C (fraction 7) then the rate of increase lessens to 514°C (fraction 22).

The increase in kinetic conversion is attributed to the increase in aromaticity of the solvent with increasing boiling point as the $^1\text{H-NMR}$ data have shown. At the equilibrium conditions, conversions increase with boiling point to about 87 percent at 400°C , then decrease to 83 percent at 500°C . The equilibrium test is designed to give a measure of donor content of the solvent and the $^1\text{H-NMR}$ data on the cyclic/alkyl aliphatic proton ratio gives a relative measure of donor content in solvents with comparable hydrogen contents. The cyclic/alkyl ratio increases from 0.56 to 1.18 as the boiling points of the solvents increase. On the other hand the total hydrogen contents of the fractions decrease from 10.26 to 6.70 percent (Table 2). The shape of the curve of equilibrium test conversions vs. boiling point is caused by two opposing factors, i.e., increasing cyclic/alkyl ratio and decreasing total hydrogen content. The net effect of these opposing factors is to produce a maximum conversion at about the $375\text{--}425^\circ\text{C}$ boiling point range.

ITSL Process Solvent Components (Battelle PNL)

Total ion GCMS chromatograms show the unusual configuration of the ITSL recycle process solvent at steady state operation. The chromatogram of the deashed SCT extract which is also known as LC-Finer feed (LCFF) represented in Figure 3 shows that the solvent has donated a large portion of his hydrogen to the coal, as few large peaks of distinguishable aromatic compounds have appeared. Among major peaks identified were phenanthrene, pyrene, chrysene and also benzo(a) pyrene and anthathrene. These compounds seem to grow dominant as the solvent recycles and its hydrogen donor quality improves. The LCFF stream is hydrotreated in the second stage LC-Finer and converted to Total Liquid Product (TLP). The GCMS chromatogram of TLP is shown in Figure 4 in which the major peaks disappear, more likely due to conversion of the parent hydrocarbons to a variety of hydrogenated derivatives, except for the pyrene peak, which is only slightly hydrogenated.

Conclusion

The peculiar behaviour of polyaromatic hydrocarbons under catalytic hydrogenation/hydrocracking condition, leads to a variety of speculative thoughts on the role of each individual variety in coal liquefaction.

On the basis of preliminary data some tentative statements and speculative thoughts are presented below with the particular objective of guiding further experimental studies on the nature of the ITSL process recycle solvent at equilibrium:

- o The ITSL equilibrium process solvent is largely constituted by a few major polyaromatic hydrocarbons and related hydrogenated moieties.
- o The possibility exists now to reproduce the ITSL equilibrium process solvent by using few model compounds, i.e., hydrogenated phenanthrenes, chrysene and perhaps pyrene and their alkyl derivatives.
- o Reacting the above model solvents of different hydrogen contents with aromatic model compounds representing coal as hydrogen acceptor e.i., anthathrene and pyrene and their alkyl derivatives, a researcher can better simulate the reaction between the actual solvent and the coal.
- o Practically all the hydrogen is very rapidly donated by the process solvent and very little, if any, via hydrogen gas. Consequently, the SCT coal extraction should not be affected by gas-slurry flow-dynamics and in turn bench-scale and scale-up operations should have excellent correlation, as one of the major differences is removed.

Acknowledgment

The authors appreciate the technical support of Dr. Harvey Schindler of The Lummus Company, Mr. John Potts of Cities Service Research and Development Company and Dr. Martin Neuworth of Mitre Corporation.

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Figure 1
Integrated Two Stage Liquefaction PDU
Current Process Flowscheme

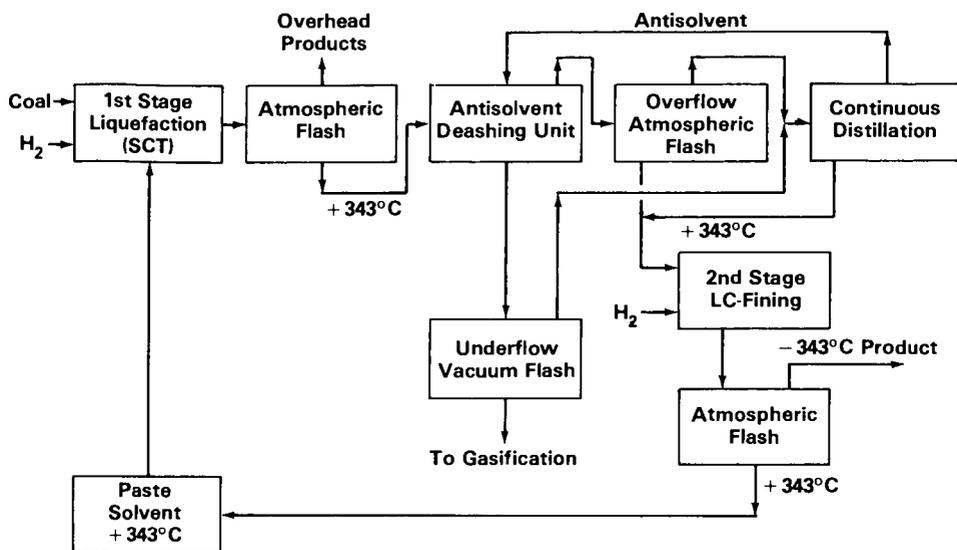


Figure 2
Microautoclave Tests with Fractions

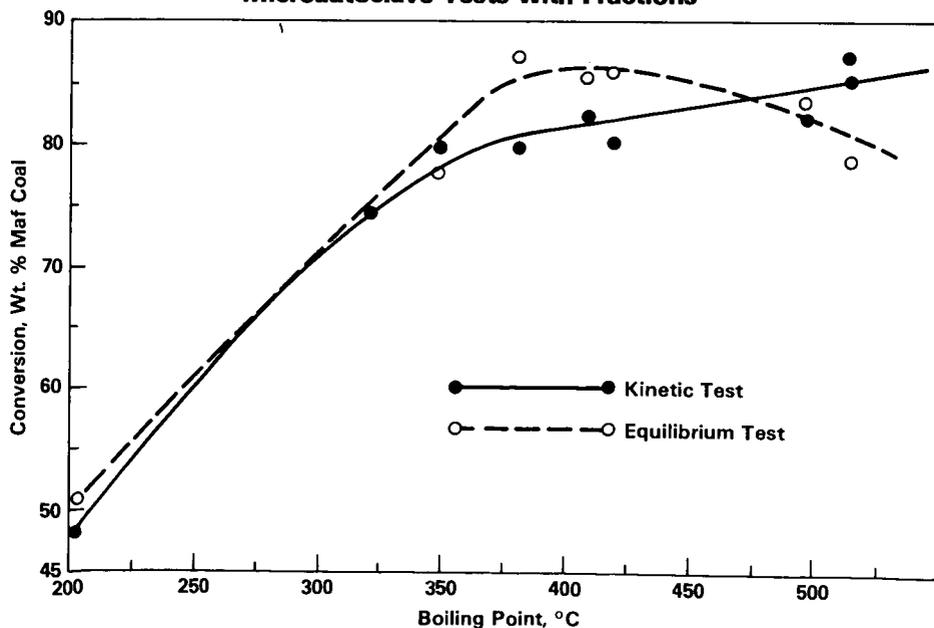


Figure 3

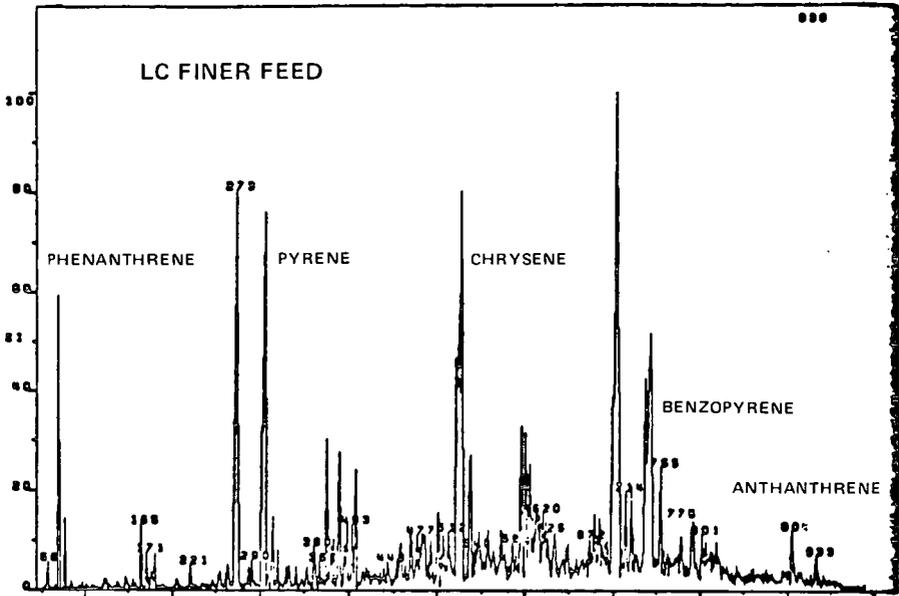


Figure 4

