

CATALYST SPECIFICITIES IN HIGH PRESSURE HYDROPROCESSING
OF PYROLYSIS AND GASIFICATION TARS

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ABSTRACT

Over a period of several years [1], the Department of Forest Science at Texas A&M University has been conducting studies in the hydroprocessing (catalytic high pressure hydrotreating or hydrodeoxygenation accompanied by hydrocracking) of pyrolytic tars produced in biomass pyrolysis and gasification. Upgrading through hydroprocessing results in good yields of volatile hydrocarbon and phenolic products. This paper compares the performance of twenty different catalysts selected for hydroprocessing of a pine pyrolysis oil, describes the use of noble metal catalysts with tars produced from nine different biomass feedstocks (oil from pine pyrolysis and the tars from pine wood chip, pine plywood trim, pecan shell, peanut shell, sugarcane bagasse, corncob, rice hull, and cottonseed hull gasification), and compares the use of several catalysts in a trickle bed reactor for kinetic studies of the hydroprocessing reaction.

METHODOLOGY

Feedstock and Materials. Pine pyrolytic oil produced by Tech-Air Corporation from sawdust and bark in the Cordele GA demonstration plant was used as the base oil in this study. A barrel of this oil was generously provided by American Can Company. Other tars from agricultural residues were produced in a modified gasification-pyrolysis reactor (100 kg capacity updraft gasifier run under conditions to promote tar production).

Catalysts used for the batch reactor studies were used in the form purchased from Strem, Harshaw, or donated by UOP (Table 1). For the trickle bed reactor studies, the 5% Pt/Al₂O₃ powder catalyst was mixed with Ludox AS-40 binder in proportions that the final catalysts contained 30% SiO₂. A paste was made when the binder was added, and this paste was taken up into a syringe with a 1/16 inch plunger. The catalysts was extruded, dried and calcined in air at 756°K (483°C) for four hours. In order to obtain an active catalyst, the Pt/Al₂O₃ pellet was reduced *in situ* prior to the experiments. The reduction was done by passing H₂ through the catalytic bed at 673°K, 8270kPa at a flow rate of 200 cm³/min (21.1°C, 1 atm) for one hour.

For Harshaw's catalysts, the sulfided form was used. Presulfiding of the catalysts was done *in situ* prior to the experiments. A mixture of 90% H₂ and 10% H₂S by volume was passed through the catalyst bed at a flow rate of 40 cm³/min (measured at 21.2°C, 1 atm) at 673°K and atmospheric pressure until the outlet gas showed no further sign of H₂S consumption.

Decahydronaphthalene (decalin) purchased in purified grade from Fisher Scientific and methyl cyclohexane produced by hydrogenation of toluene were used as hydrogen-donor solvents in the hydroprocessing reactions.

Batch Reactor Studies. Some twenty catalysts (Table I) were used in preliminary screening studies [2,3]. A number of experiments were conducted using the various catalysts at differing reaction conditions in attempts towards optimization for each catalyst, but the results obtained could not be tabulated to effect some ranking order. Standard conditions chosen were those found to be effective for the 5% Pd and 5% Pt catalysts in the preliminary study - 60g stripped pine pyrolytic tar (water removed through azeotropic distillation with toluene), 100g solvent (decalin or methyl cyclohexane), 20g catalyst, 1000 psi (@ ambient temp.) hydrogen feed and 400°C for 60

minutes in a rocking reactor (Aminco 4 3/8 inch o.d. series, 1500 ml capacity, rated at 5500 psi). After the reactions, the following were calculated (Tables II and III): *hydrocarbon conversion %* (total liquid product corrected for solvent and water concentrations), *water yield %* (water produced as % of pyrolytic tar feed - a measure of hydrotreating or hydrodeoxygenation activity), *gases and losses %* (balance of products by difference as % of pyrolytic tar feed - a measure of excess hydrocracking activity in the production of gaseous hydrocarbons). For a few catalysts with limited catalytic activity, a fourth component of the reaction product was calculated: *tar residue %*. Tar residue is the heavy tar deposited on catalysts and insoluble in the reaction solvent selected (determined by weighing dirtied catalyst after reaction, subtracting weight of catalyst used, and expressing as % of pyrolytic tar feed).

Trickle-bed Reactor Studies. A schematic for the trickle-bed reactor system is shown in Figure 1 [4,5]. The reactor proper consists of a 32-inch long 316 SS tube, 3/4 inch O.D., 0.065 inch thick. The bottom 12 inches contained an inert support, Pyrox 3 mm dia. glass beads, with the top 20 inches packed with catalyst. The reaction temperature was non-isothermal, viz. 22 inches of the reactor was immersed in a salt bath (Hotec heat transfer salt, a mixture of 53% potassium nitrate, 40% sodium nitrite, 7% sodium nitrate; air bubbled through bath to ensure uniform temperature profile), so that the salt around the bottom half of the catalyst bed (10 in) was at temperature, while the temperature of non-immersed top half decreased linearly from near reaction temperature at the top of the salt bath to 190°C at the top of the reactor. By using non-isothermal conditions, the temperature inside the reactor increased gradually along the reactor length, preventing the volatiles in the pine pyrolysis oil from flashing into the gas phase suddenly. With the catalyst packed at the top of the reactor, the pyrolysis oil was hydrotreated before the oxygen-containing compounds could polymerize at high temperature. The NiW catalyst is a strong cracking catalyst and was thus not effective in hydrotreating: oxygen-containing components in the oil polymerized in the reactor.

Under typical operating conditions, H₂ feed was 100 cc/min (at 60°C, 1 atm) per gram of pine pyrolysis oil input; liquid feed was used at a ratio of 2 grams decalin per gram of pine pyrolysis oil; weight hourly space velocity (g oil input per hr / g catalyst in the reactor) was 0.5 to 3.0 hr⁻¹; salt bath temperature was 673 to 673°K; H₂ pressure was 5272 to 10443 kPa (750 to 1500 psig); and, catalyst bed was 60 g. for each load. After the reaction, the catalyst was regenerated by burning in air to remove coke deposited on the catalyst during the reaction, then reactivated for the next run.

Sample and Product Chemical Analyses. Analytical techniques used to determine the chemical composition of raw oils and hydroprocessed products are given elsewhere in this volume [6].

RESULTS AND DISCUSSION

Batch Reactor Studies. Results for the 20 catalysts using the batch rocking reactor using decalin as hydrogen-donor solvent are given in Table II; those for the methyl cyclohexane solvent system in Table III. The 5% noble metal catalysts in both solvent systems generally gave superior results in hydrocarbon conversion and water yield. Note that hydrocarbon conversion efficiencies may appear low because these are expressed on a mass and not energy basis. With 27% oxygen content in the raw pyrolytic tar feed, maximum hydrocarbon conversion is 73% plus hydrogen uptake; maximum water yield is 30% (27 X 18/16). These data will be discussed in the oral presentation.

Trickle-bed Reactor Studies - Oxygen Removal. The effect of reaction temperature, pressure and space velocity on oxygen removal (hydrotreating, hydrodeoxygenation) are shown in Figures 2 through 4. The points in the figures are the experimental data and the solid lines were evaluated by using an oxygen removal model. A clear trend is observed for the effect of reaction temperature and pressure, while changes in space velocities did not affect oxygen removal. The Pt/Al₂O₃ catalyst exhibits the best activity for oxygen removal for pine pyrolysis oil among the four catalysts tested. The NiW catalyst was not effective in oxygen removal, and was dropped from further consideration.

Trickle-bed Reactor Studies - Kinetic Modeling. The proposed kinetic model for hydroprocessing pyrolysis oil consists of the kinetic scheme as shown in Figure 5. Terms used in this and subsequent figures are defined as follows (see other paper in this volume [6] for examples of the GPC chromatograms):

<i>heavy nonvolatiles</i>	- nonvolatiles in GPC fractions 1 and 2.
<i>light nonvolatiles</i>	- nonvolatiles in GPC fractions 3 and 4
<i>phenols</i>	- volatiles in GPC fraction 3 detectable by GC
<i>aromatics</i>	- volatiles in GPC fractions 4 and 5, excluding solvents
<i>alkanes</i>	- volatiles in GPC fraction 2
<i>coke + H₂O + outlet gases</i>	- 1 minus liquid yield
<i>liquid yield</i>	- $\frac{\text{(wt. of fractions by GPC)} - \text{(solvents in hydroprocessed oil)}}{\text{pine pyrolysis oil input}}$

An elaboration of the kinetic model is outside the scope of this preprint. The outcome, expressed as experimental and predicted values of the lumped species in the kinetic model at various reaction conditions (temperature, pressure and space velocity effects) is presented in Figures 6 through 14.

Effect of Reaction Temperature (Figures 6 to 8). Temperatures selected for study were 623, 648 and 673°K. All reactions were run at 8720 kPa and WHSV 2 hr⁻¹.

Effect of Reaction Pressure (Figures 9 to 11). The effect of reaction pressure was evaluated at 5272, 6996, 8720 and 10443 kPa at 673°K and WHSV 2 hr⁻¹.

Effect of Space Velocity (Figures 12 to 14). WHSV was evaluated at 0.5, 1.0, 2.0 and 3.0 hr⁻¹. Pressure used was 8721 kPa; temperature, 673°K.

Results are essentially self-evident in these figures, but will be discussed in detail in the oral version and final manuscript of this communication.

ACKNOWLEDGMENTS

This research has been generously supported by the Texas Agricultural Experiment Station, the Center for Energy and Mineral Resources and the College of Agriculture, all parts of the Texas A&M University System, and by two USDA Special Research Grants (Agreements 59-2481-0-2-089-0 and 59-2481-1-2-123-0).

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- [2] E.J. Soltes, "Diesel Fuels from Pine Pyrolytic Oils". Final Report, USDA Energy Grants FY1980 No. 59-2481-0-2-089-0 (1982).
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- [5] Y-H.E. Sheu, *Kinetic Studies of Upgrading Pine Pyrolytic Oil by Hydrotreatment*, Ph.D. Dissertation, Chemical Engineering, Texas A&M University, May 1985.
- [6] E.J. Soltes and S-C.K. Lin, "Chromatography of Non-Derivatized Pyrolysis Oils and Upgraded Products", THIS volume.

TABLE I.

CATALYSTS SCREENED FOR HYDROTREATING AND HYDROCRACKING OF BIOMASS THERMOCHEMICAL TARS

5% Pd/alumina	2% Pt/alumina	0.5% Pd/alumina
5% Pd/carbon	5% Pt/alumina	0.5% Pt/alumina
5% Re/alumina	5% Pt/carbon	0.5% Re/alumina
5% Rh/alumina	Harshaw CoMo-0603	silicated gamma alumina
5% Ru/alumina	Harshaw HT-400	NiO-WO ₃ / silica alumina
Raney Ni	Harshaw Ni-4301	UOP Lomax
NiCO ₃	ZrO ₂ on alumina	UOP Unibon

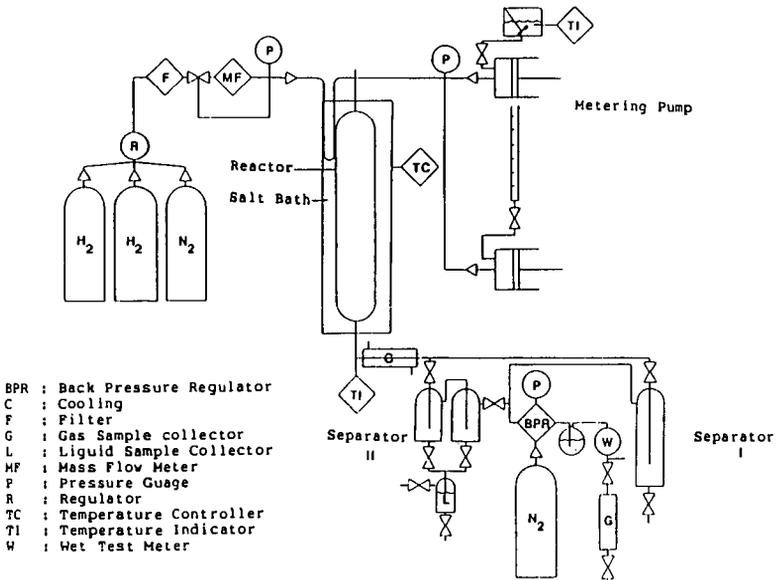


Figure 1. Schematic process of trickle-bed reactor system

TABLE II. HYDROPROCESSING OF TECH-AIR PINE PYROLYSIS OIL IN DECALIN SOLVENT¹

Catalyst Type	Hydrocarbon Conversion ² %	Water Yield ² %	Tar Residue ² %	Gases & Losses ² %
5% Pd/alumina	55.7	25.3	-	19.0
5% Pd/carbon	35.7	21.7	-	42.5
5% Pt/alumina	44.5	24.5	-	31.0
5% Pt/carbon	33.1	17.7	-	49.2
5% Rh/alumina	39.3	15.8	-	44.8
5% Ru/alumina	25.8	20.0	-	54.2
5% Re/alumina	44.3	18.2	-	37.5
UOP Lomax	43.5	8.3	-	48.2
UOP Unibon	33.3	6.6	-	60.1
Raney Ni	40.1	19.6	-	40.3
2% Pt/alumina	51.4	5.0	-	43.6
0.5% Pd/alumina	18.4	9.8	-	71.2
0.5% Pt/alumina	25.7	10.8	-	63.5
0.5% Re/alumina ³	-	10.1	75.4	-
Ni-4301	11.9	8.3	40.3	39.5
CoMo-0603	4.2	6.0	41.2	48.6
HT-400	3.4	7.5	57.9	31.2
ZrO ₂	25.1	7.4	35.9	31.6
silica alumina	3.3	13.2	69.9	13.6
silicated gamma alumina	11.4	6.7	45.3	36.6

¹ conditions as described in text

² defined in text

³ hydrocarbon conversion very small; gases and losses % could not be calculated

TABLE III. HYDROPROCESSING OF TECH-AIR PINE PYROLYSIS OIL IN METHYL CYCLOHEXANE SOLVENT¹

Catalyst Type	Hydrocarbon Conversion ² %	Water Yield ² %	Tar Residue ² %	Gases & Losses ² %
5% Pd/alumina	54.5	8.9	-	36.6
5% Pd/carbon	37.4	8.2	-	54.5
5% Pt/alumina	44.2	5.0	-	50.8
5% Pt/carbon	19.1	6.7	-	76.5
5% Rh/alumina	38.9	16.6	-	44.5
5% Ru/alumina	24.9	12.4	-	62.8
5% Re/alumina	37.1	20.0	-	42.8
UOP Lomax	38.0	5.0	-	57.0
UOP Unibon	35.6	7.5	-	56.9
Raney Ni	40.1	19.1	-	40.1
2% Pt/alumina	21.3	2.4	-	76.3
0.5% Pd/alumina	53.9	8.9	-	37.2
0.5% Pt/alumina	46.5	10.1	-	43.3
0.5% Re/alumina ³	-	5.0	69.3	-
Ni-4301 ³	-	10.0	50.2	-
CoMo-0603 ³	-	4.8	46.6	-
HT-400 ³	-	8.3	60.6	-
ZrO ₂ ³	-	5.0	63.4	-
silica alumina ³	-	12.4	74.0	-
silicated gamma alumina ³	-	1.7	61.7	-

¹ conditions as described in text

² defined in text

³ hydrocarbon conversion very small; gases and losses % could not be calculated

TABLE V. SPECIFICATIONS FOR THE CATALYSTS USED IN THE TRICKLE BED REACTOR STUDY¹

Catalyst Type	Pt/Al ₂ O ₃	CoMo	NiMo	NiW
Manufacturer	Strem 78-166	Harshaw HT-400	Harshaw HT-500	Harshaw Ni-4301
Size	powder	1/16" E. ²	1/16" E. ²	1/16" E. ²
Composition	5% Pt	3% CoO, 15% MoO ₃	3.5% NiO, 15.5% MoO ₃	6% Ni, 19% W ³
Surface Area, m ² /g	100 ³	200	200	230
Pore Volume, cc/g	0.52 ³	0.45	0.46	0.37
Pore Size, dia, Å	100	94	88	104

¹ conditions as described in text

² E. = extrudate

³ for the pellet catalyst

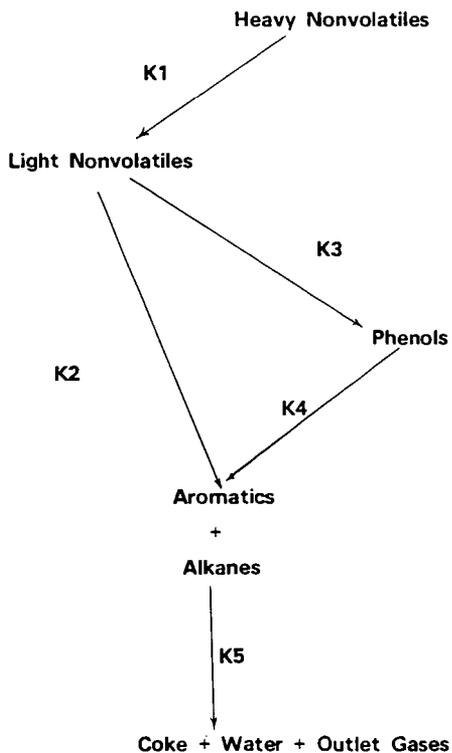


FIGURE 5. Lumped Kinetic Scheme

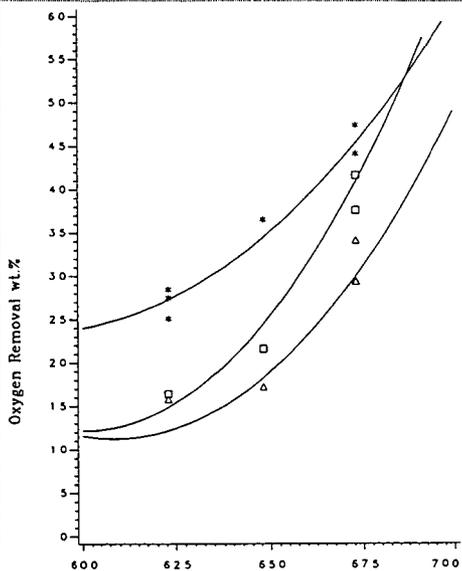


FIGURE 2 - Reaction Temperature, K

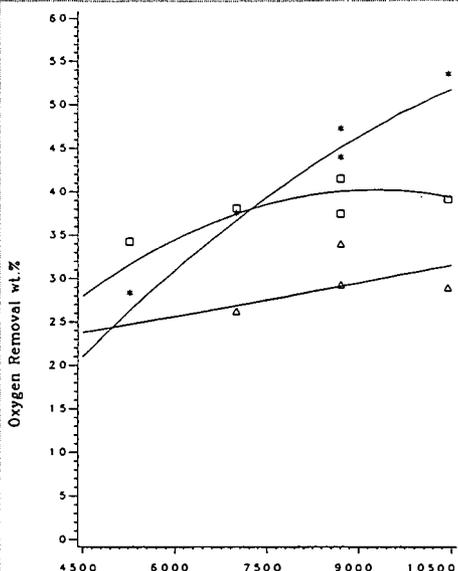


FIGURE 3 - Reaction Pressure, kPa

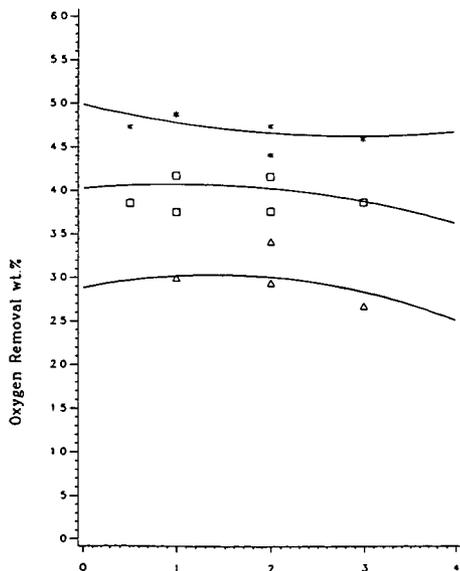


FIGURE 4 - Space Velocity, hr⁻¹

Effects of Reaction Temperature, Reaction Pressure and Space Velocity on Oxygen Removal - Trickle-Bed Reactor Study

- * Pt catalyst
- CoMo
- △ NiMo
- Model Predictions

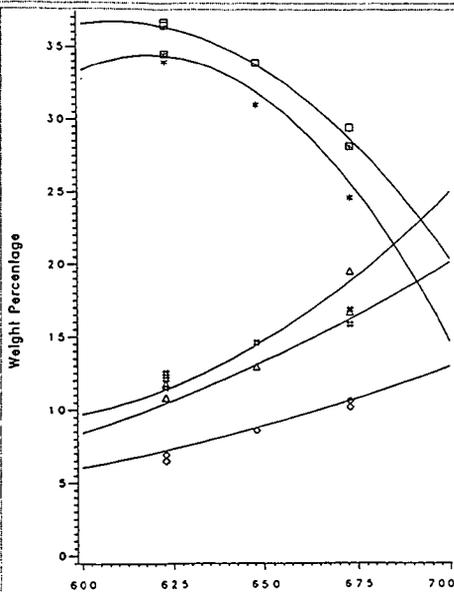


FIGURE 6 - Pt/Al₂O₃ Catalyst

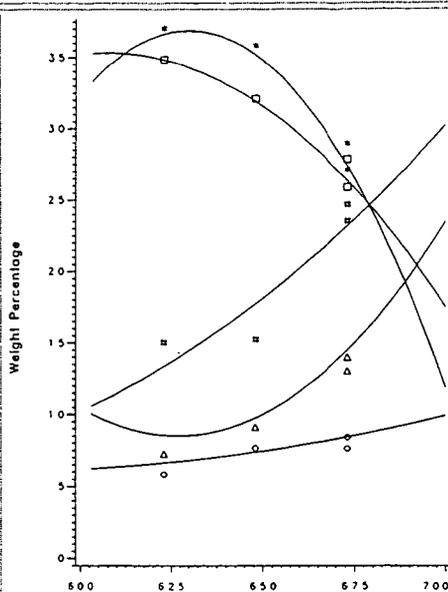


FIGURE 7 - CoMo Catalyst

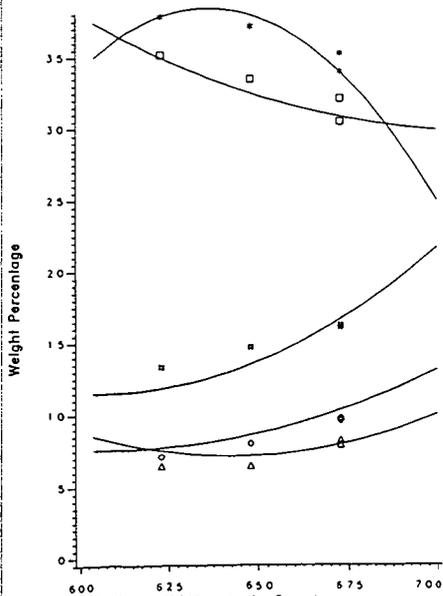


FIGURE 8 - NiMo Catalyst

Effects of Reaction Temperature, K_1 on Hydroprocessing - 8720 kPa, WHSV 2 hr⁻¹ Trickle-Bed Reactor Study

- * Heavy Nonvolatiles
- Light Nonvolatiles
- Phenols
- △ Aromatics + Alkanes
- Coke + Water + Outlet Gases
- Model Predictions

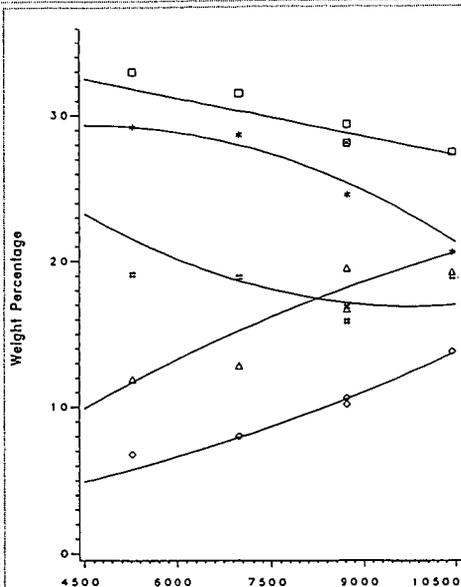


FIGURE 9 - Pt/Al₂O₃ Catalyst

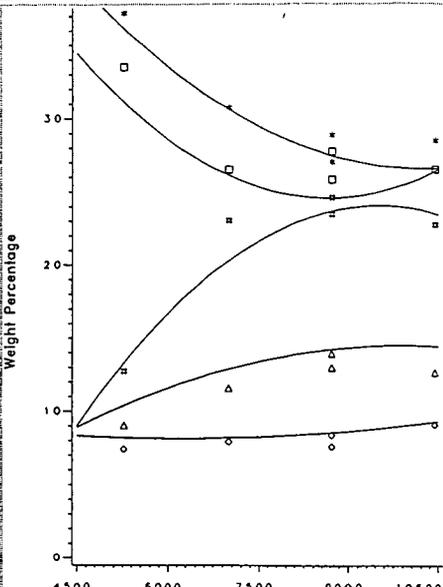


FIGURE 10 - CoMo Catalyst

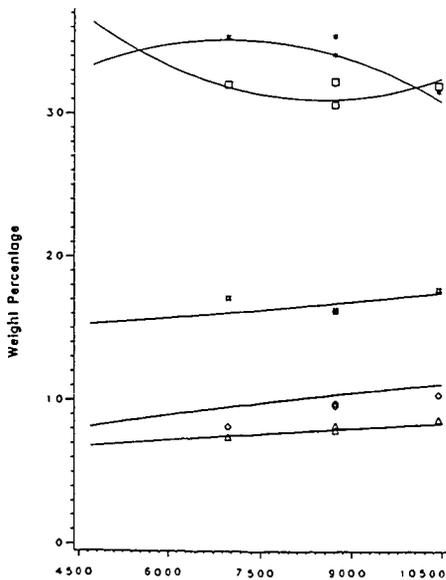


FIGURE 11 - NiMo Catalyst

Effects of Reaction Pressure, kPa, on Hydroprocessing - 673 K, WHSV 2 hr⁻¹ Trickle-Bed Reactor Study

- Heavy Nonvolatiles
- ◻ Light Nonvolatiles
- ◊ Phenols
- △ Aromatics + Alkanes
- Coke + Water + Outlet Gases
- Model Predictions

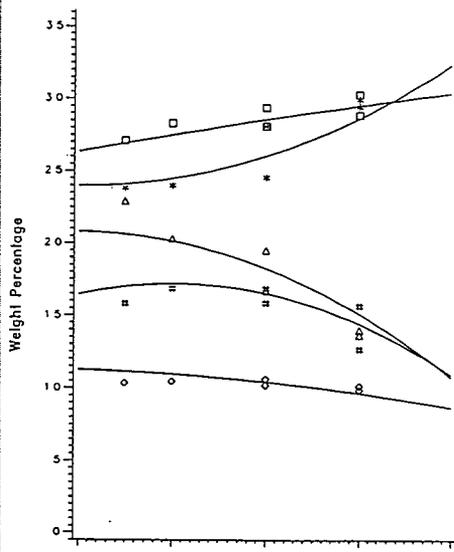


FIGURE 12 - Pt/Al₂O₃ Catalyst

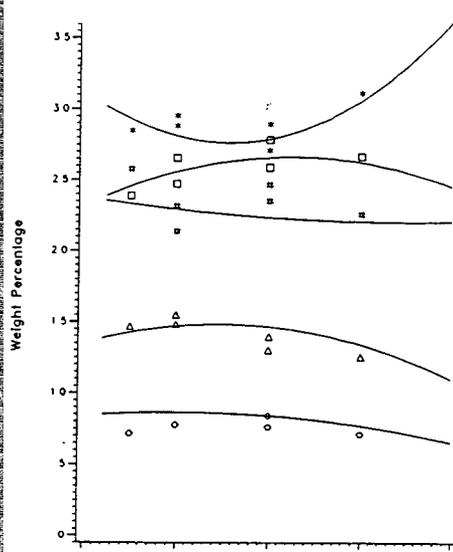


FIGURE 13 - CoMo Catalyst

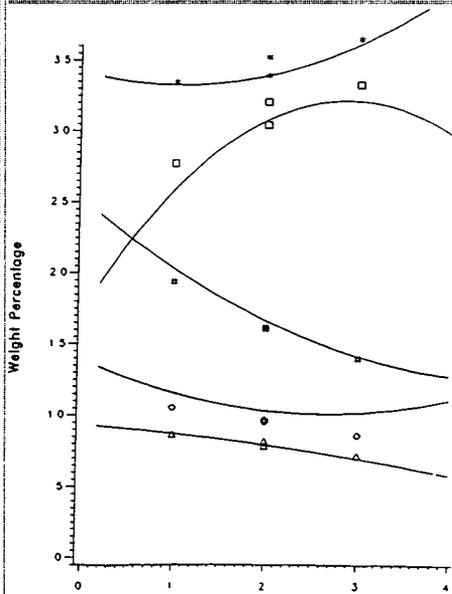


FIGURE 14 - NiMo Catalyst

Effects of Space Velocity,
hr⁻¹, on Hydroprocessing -
8720 kPa, 673 K
Trickle-Bed Reactor Study

- Heavy Nonvolatiles
- Light Nonvolatiles
- Phenals
- △ Aromatics + Alkanes
- Cake + Water + Outlet Gases
- Model Predictions