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LOW SEVERITY UPGRADING OF F-T WAXES WITH SOLID SUPERACIDS

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SUMMARY

During the last quarter isomerization and hydrocracking of n-hexadecane were carried out in a continuous flow fixed bed reactor described in a previous report. Test runs showed that the temperature and pressure in this reactor can be controlled to within $\pm 1^\circ\text{C}$ and ± 2 psig, respectively. The reaction conditions were 160°C and 350 psig constant hydrogen pressure. Interestingly, product distribution from isomerization and hydrocracking of n-hexadecane conducted in this reactor is similar to that obtained from the microreactor experiments. The long-term stability of the $\text{Pt/ZrO}_2/\text{SO}_4$ catalyst was studied using this fixed bed reactor with n-hexadecane as a feedstock. Evidence was obtained that, in the presence of H_2 , the $\text{Pt/ZrO}_2/\text{SO}_4$ catalyst maintains its activity for as long as 96 hours with no evidence of deactivation.

The effect of addition of transition metals on the activity of ZrO_2/SO_4 was compared. Pt and Pd greatly enhanced the hydrotreating activity of ZrO_2/SO_4 . The activities of $\text{Pt/ZrO}_2/\text{SO}_4$, $\text{Pt/ZrO}_2/\text{MoO}_4$ and $\text{Pt/ZrO}_2/\text{WO}_4$ catalysts were also compared; it was found that the $\text{Pt/ZrO}_2/\text{SO}_4$ catalyst gave highest activity in isomerization and hydrocracking of long-chain paraffins. We also found that, even at high severity conditions, i.e., $300^\circ\text{C}/600$ psig and $250^\circ\text{C}/1200$ psig, the $\text{Pt/ZrO}_2/\text{SO}_4$ catalyst is active.

EXPERIMENTAL

A schematic diagram of the continuous flow fixed-bed reactor system used in hydrocracking of n-hexadecane was given in the February 1, 1993 through May 31, 1993 quarterly report. Before reaction, the catalyst was pressed into pellets by a hydraulic press at 20,000 psig. The pellets were then crushed and screened to obtain catalyst beads with a particle size of 20-30 mesh. The catalyst was then loaded into the hot reactor (110°C). A thermocouple was placed in the catalyst bed to record the reaction temperature. The reactor was installed into a furnace and purged with dry air at atmospheric pressure. The furnace temperature was slowly increased to 450°C with continuous flow of air. The catalyst was activated at 450°C for 1.5 hours, then cooled to room temperature under air flow. The reactor was then purged with hydrogen for five minutes and pressurized to the desired pressure. The hydrogen flow rate was established using a mass flow controller to obtain a suitable hydrogen to hexadecane molar feed ratio. The flow rate of n-hexadecane was controlled by a micropump. After establishing hydrogen and hexadecane flow rates, the furnace was turned on and a steady-state temperature of 160°C was attained in about 20 minutes. The conversion of n-hexadecane reached a steady state at approximately 40 minutes with a hydrogen flow rate of 60 ml/min and n-hexadecane of 100 cc/hr. Liquid products were taken from the product receiver and analyzed by GC (HP-5890 II).

The procedures employed in preparation of Pt/ZrO₂/MoO₄ and Pt/ZrO₂/WO₄ catalysts were similar to that of Pt/ZrO₂/SO₄ catalyst, except for the steps of incorporation of MoO₄²⁻ and WO₄²⁻ ions. Pt/ZrO₂/WO₄ catalyst was obtained by impregnating Zr(OH)₄ with aqueous ammonium metatungstate followed by evaporating water at 110°C. Platinum was impregnated

and then the catalyst was calcined in air at 800-850°C for 2 hours. Pt/ZrO₂/MoO₄ catalyst was obtained by impregnating Zr(OH)₄ with molybdic acid followed impregnating with Pt and calcining in air at 650°C. The elemental Mo and W contents in the two catalysts were each 5.0 wt%.

RESULT AND CONCLUSIONS

Catalytic Performance of Pt/ZrO₂/SO₄ Catalyst in a Continuous Flow Fixed-Bed Reactor

A comparison of product distributions obtained from hexadecane in the fixed-bed and batch reactor is shown in Figure 1. It is somewhat surprising that the product distribution obtained in the fixed-bed reactor is similar to that obtained in a batch reactor; maximum yields occurred at C₆-C₇ carbon products. The carbon number distribution is asymmetrical, perhaps because secondary cracking occurs. In a similar reactor where a Pt/Y-zeolite was used as the catalyst for hydrocracking of long-chain paraffins, a symmetrical product distribution was obtained^[1]. This difference in product distribution suggests that the classical bifunctional mechanism which is postulated to occur on zeolites may not apply to solid superacids such as Pt/ZrO₂/SO₄.

It is difficult to evaluate long period catalytic performances using a batch reactor. But with continuous flow fixed-bed reactor, long-term performance of Pt/ZrO₂/SO₄ catalyst can be tested. In 1986, Hosoi et al.^[2] reported that, for isomerization of n-butane on a Pt/ZrO₂/SO₄ catalyst in the presence of hydrogen, the catalyst maintained activity for as long as 1000 hours (150 psig, 200°C). It is not known if the Pt/ZrO₂/SO₄ catalyst will behave similarly in upgrading of long-chain paraffins. Results shown in Figure 2 demonstrate the long term activity duration for upgrading of n-hexadecane. The reaction rate varied between 8.0 and 9.0 grams

of n-hexadecane converted per hour per gram catalyst, which is twice as much as obtained from the microreactor at the same temperature and pressure. The activity of the Pt/ZrO₂/SO₄ catalyst after 96 hrs is still comparable to its initial activity; the product distribution and the ratio of multi/mono branched paraffins remain unchanged as the reaction proceeds.

Effect of Transition Metal Addition on the Activity of ZrO₂/SO₄

In the absence of metals with a hydrogenation ability, the initial activity of ZrO₂/SO₄ catalyst in hydrocracking of long-chain paraffins was high but deactivation occurred rapidly. It was assumed that the deactivation was caused by the formation of coke precursors on strong acid sites since coke was detected in the used catalyst^[2]. To promote the hydrogenation of coke precursors, Pt, a good hydrogenation catalyst was incorporated into ZrO₂/SO₄ and its effect in promoting isomerization and hydrocracking of long-chain paraffins was studied. The function of Pt on ZrO₂/SO₄ is not only to hydrogenate coke precursors, but it appears to generate protonic acid sites.

As shown in Figure 3, the effects of nine transition metals having a hydrogenation function were compared. Metal loadings were 0.5 wt% for Pt, Pd, and Ru, 2.0 wt for Ni and 5.0 wt% for Mo, W, Fe, Sn, and Mn/Fe. It is clear that, among these metals, Pt and Pd show the highest activity, even though other metals have higher loadings. The high activity achieved with Pt and Pd is ascribed to their ability to dissociate molecular hydrogen to form protonic acid sites and to generate hydrides responsible for the saturation of coke intermediates. This finding was supported by in-situ FT-IR analysis.

Activity of Sulfate, Molybdate and Tungstate Treated Pt/ZrO₂

The Pt/ZrO₂/SO₄ catalyst is characterized by its strong acidity because the SO₄²⁻ anion

withdraws electrons from ZrO_2 , leaving an electron-deficient center which may function as a Lewis acid site. The Lewis acid sites can become protonic acid sites in the presence of water or molecular hydrogen.

We have also succeeded in synthesizing other types of superacids, ones not containing any sulfate ion. These catalysts are ZrO_2 promoted with anions of MoO_4^{2-} and WO_4^{2-} . It was reported that these two catalysts were as active in isomerization of n-butane and n-pentane as $\text{ZrO}_2/\text{SO}_4^{[3]}$. However, for isomerization and hydrocracking of long-chain paraffins, such as n-hexadecane, significant differences were found among these catalysts. As shown in Figure 4, maximum activity is observed with SO_4^{2-} promoted catalysts while the other two catalysts give very low activity in cracking of n-hexadecane. The catalytic activity of zirconium solid superacids depends greatly on the type of anion and proper incorporation of the anion into the ZrO_2 tetragonal structure. The structural interaction between the different anions and ZrO_2 will be studied.

Behavior of Pt/ ZrO_2 / SO_4 Catalyst under Conditions of High Severity

A significant characteristic of Pt/ ZrO_2 / SO_4 catalyst is its high activity in isomerization and hydrocracking of long-chain paraffins under mild conditions. We have not known whether the catalyst will decompose at high pressure or temperature, since coordination between SO_4 and ZrO_2 may be relatively unstable at high severity. We therefore carried out the isomerization and hydrocracking of n-hexadecane at 1600 psig and 160°C and found that n-hexadecane was isomerized and hydrocracked completely after 30 minutes. As shown in Figure 5, the product from isomerization and hydrocracking of n-hexadecane contains mainly C_5 - C_8 isoparaffins, indicating that deep cracking is the main event under such conditions. No deactivation was

observed during the reaction.

FUTURE WORK

Characterization of ZrO_2/SO_4 -based catalysts using TPD coupled with FT-IR analysis will be used to gain insight into the chemistry of isomerization and hydrocracking of long-chain paraffins and waxes. Specifically, the catalytic activity of Pt and Ni promoted ZrO_2/SO_4 catalyst will be evaluated and related to their ability to dissociate molecular hydrogen.

The effect of aromatic compounds on product distribution in isomerization and hydrocracking of long-chain paraffins will be investigated in the continuous flow fixed-bed reactor.

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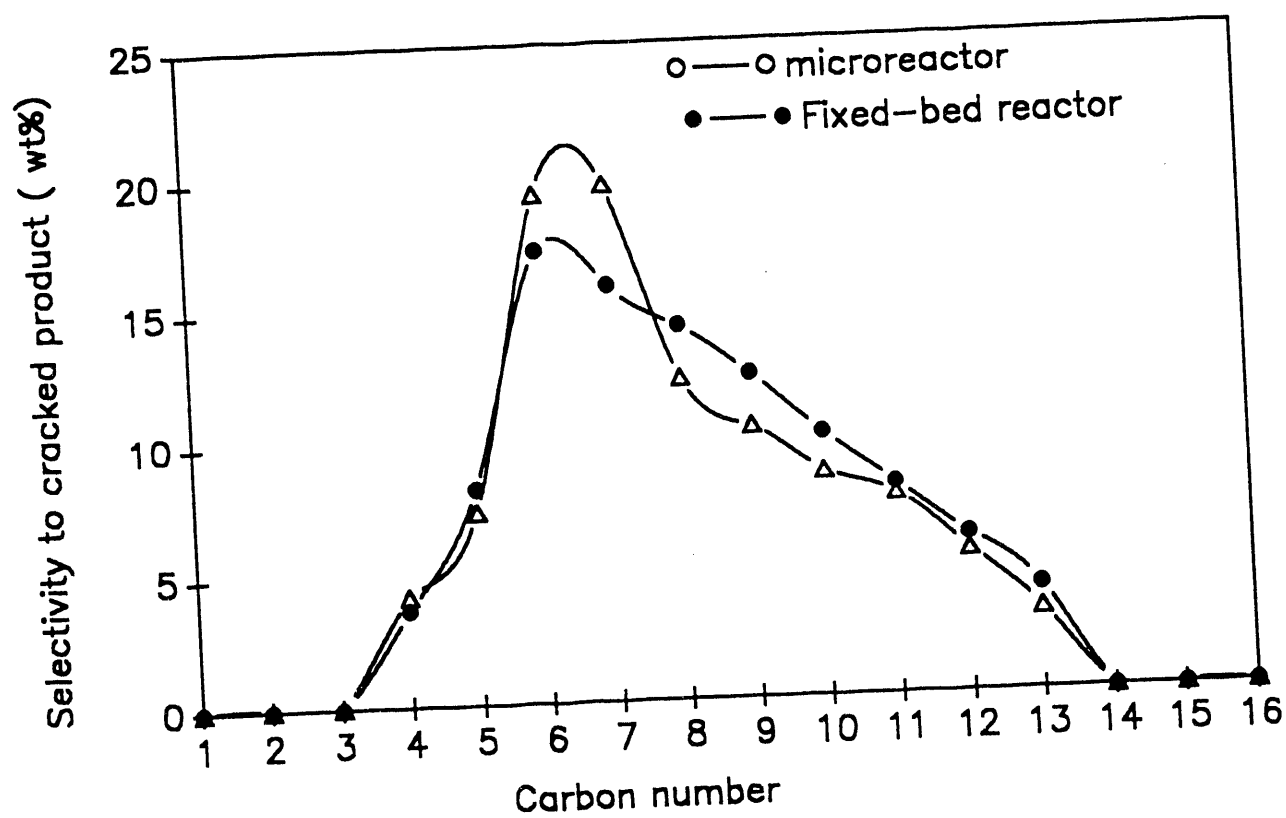


Figure 1. Comparison of product distribution from the upgrading of n-hexadecane in a fixed-bed reactor(160°C, 350 psig, $H_2/n-C_{16}=5.7$) and a microreactor(160°C, 350 psig, 60 min).

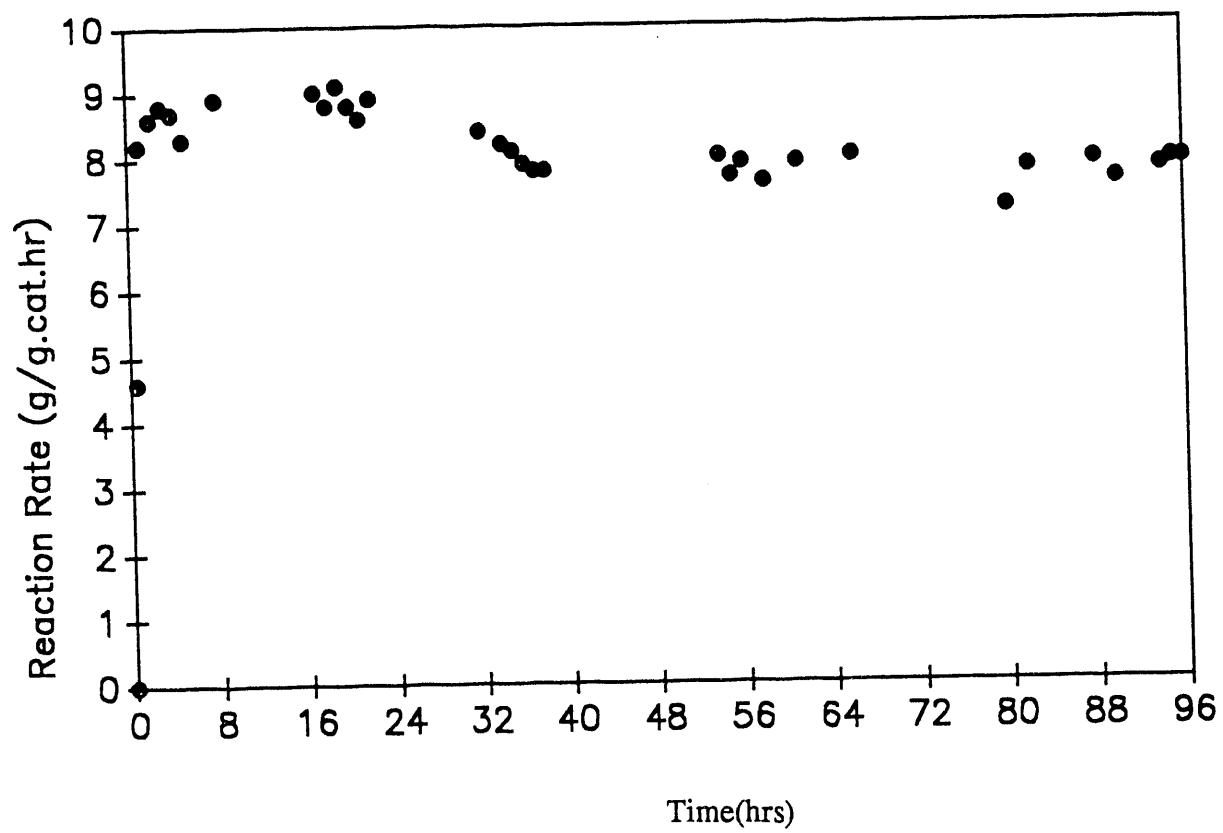


Figure 2. Long-term performance of Pt/ZrO₂/SO₄ catalyst in a fixed-bed reactor.

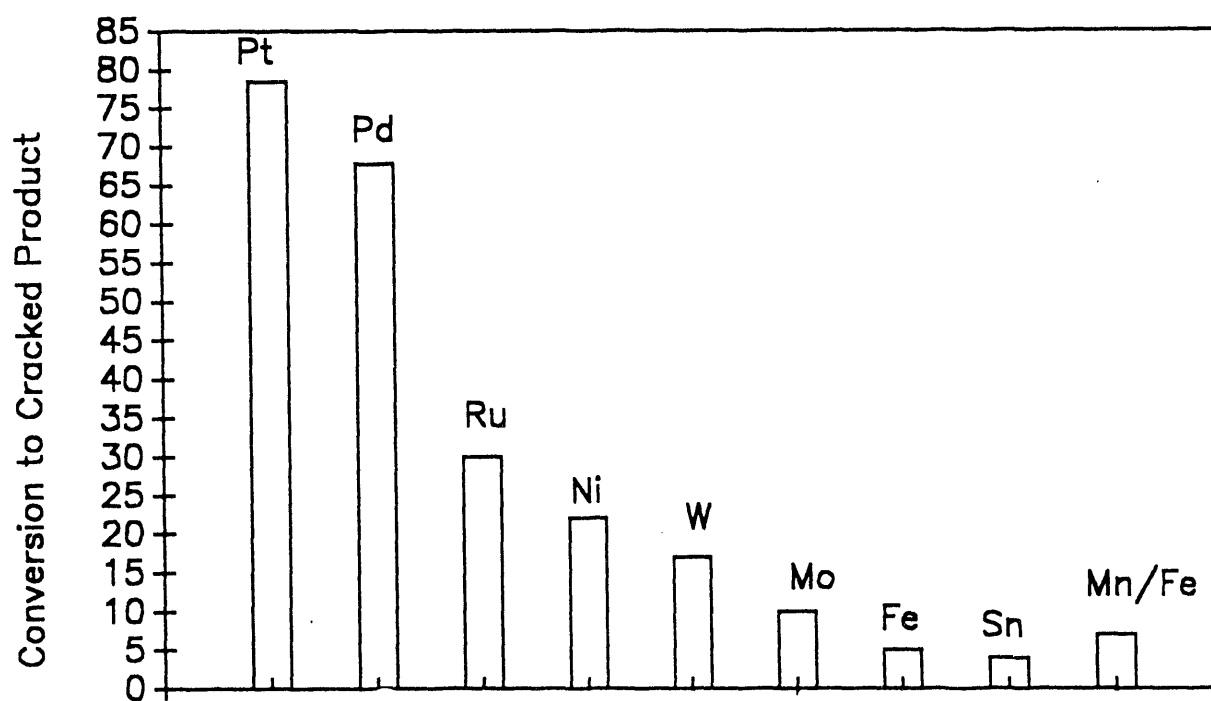


Figure 3. Effect of addition of transition metal on the activity of ZrO_2/SO_4

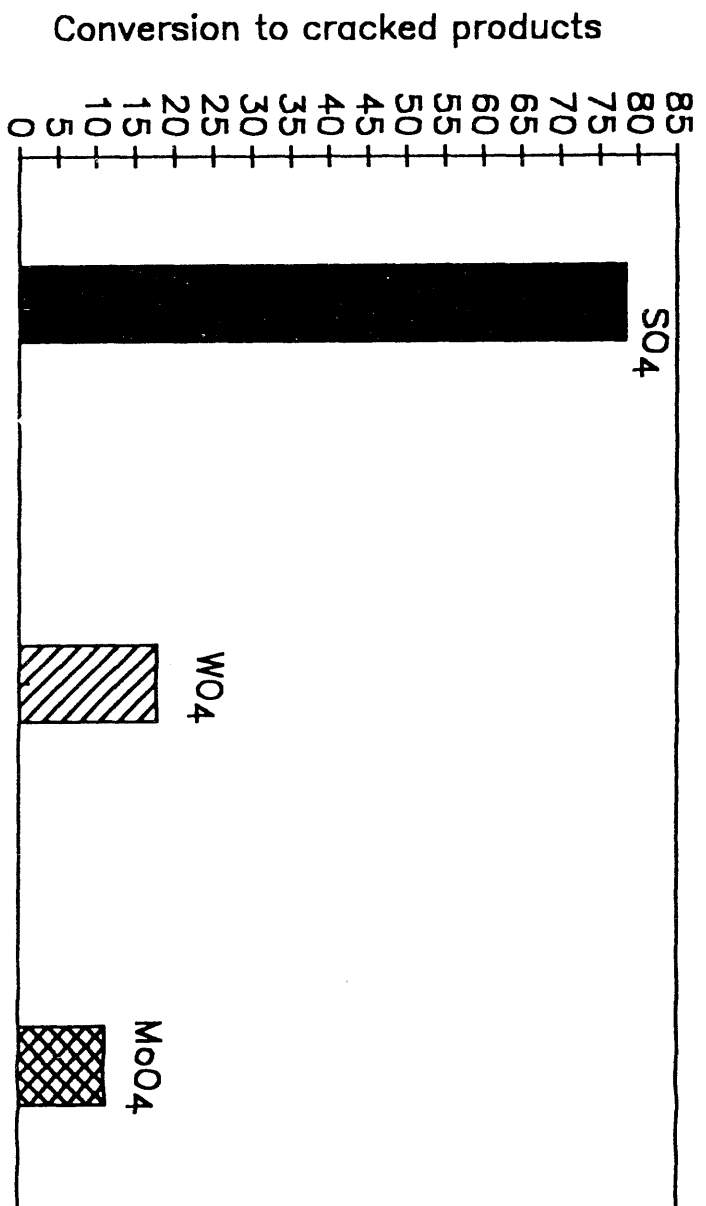


Figure 4. Activity of different anion-treated Pt/ZrO₂ in upgrading of n-hexadecane

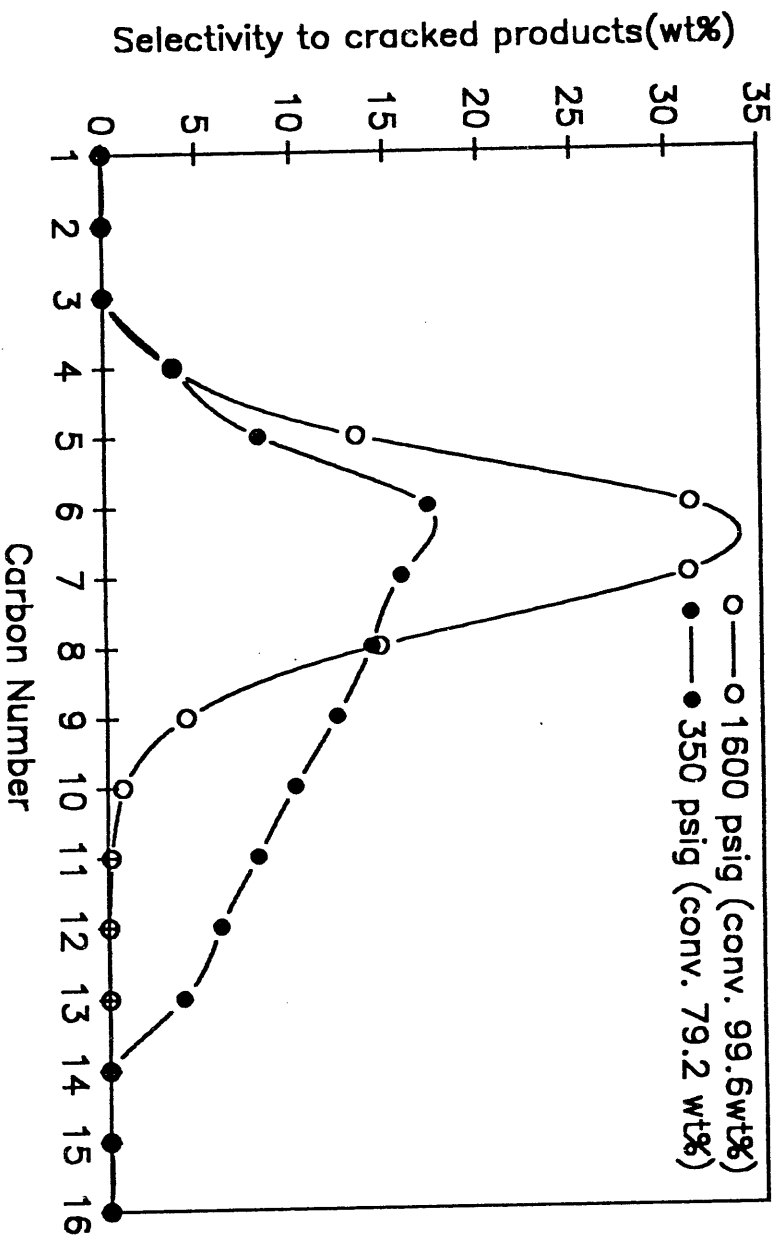


Figure 5. Effect of hydrogen pressure on product distribution.

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