Hydrogenation of F-T Products and Polyolefins to Environmentally Clean High Cetane Diesel Fuels, Jet Fuels and Lube-based Oils.

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Previous research in this laboratory investigated the activity of a platinum-promoted zirconia catalyst, $Pt/ZrO_2/SO_4$, for the isomerization of n-heptane and n-hexadecane. These catalytic systems, however, lost activity due to the loss of sulfur from the catalyst. We then found that the substitution of tungsten trioxide (WO_3) for SO_4 resulted in a more stable and selective catalyst for the hydroisomerization of n-hexadecane.

Laboratory work was then carried out successfully in a small continuous trickle-bed reactor using a $Pt/ZrO_2/WO_3$ catalyst. A 90 wt% iso-C_{16} selectivity and a 71wt% iso-C_{16} yield were achieved at 79 wt% conversion of hexadecane. The objective in the last half-year has been to extend research to the conversion of paraffins longer than hexadecane, such as those produced in the F-T process, to a variety of clean transportation fuels. This was carried out using the stable and selective $Pt/ZrO_2/WO_3$ catalyst to hydroisomerize and hydrocrack pure compounds, namely n-C_{16}, n-$C_{20,}$ n-C_{24}, n-C_{28} and their mixtures, representative of alkane chains found in F-T products.

Catalytic activity tests were carried out in a 27 ml micro autoclave system. In a typical reaction, 0.25 g of the catalyst was activated at 450ºC for 40 minutes in air and then charged into a microreactor that was predried overnight. After loading the catalyst, the reactant (typically 3 g) was charged. The reactor was cooled to room temperature and hydrogen added to 500 psi (cold) in all reactions. The reactor was shaken horizontally at 200 rpm. A computer was used to record the reaction pressure, temperature and time during the reaction. The reaction was terminated by cooling to room temperature.

Since the catalyst and reactants were chosen, the remaining reaction variables are reaction time, reaction temperature, hydrogen pressure, and hydrocarbon/catalyst ratios. Only the effects of reaction time and reaction temperature on product distributions were studied. The effect of hydrogen pressure was not studied because it is known that conversion decreases with increasing hydrogen pressure for platinum-promoted tungstate-modified zirconia catalysts.

A typical GC chromatogram for the reaction of n-C_{28} and the product fuel ranges are shown in Figure 1. Selectivity was calculated by dividing the total weight in the desired product range by the conversion of the reactant. Yield is defined as the ratio of the selected product range to the amount of reactant in the feed.

Figure 2 shows yield-product distribution graphs at three different conversions for octacosane (C_{28}) at 220°C. It illustrates the yields to fuel ranges with increasing conversion. Figure 2-a is at 79% conversion, Figure 2-b at 92% conversion and Figure 2-c at 99% conversion. The lube-base oil yield is highest at 79% conversion and consists of only branched isomers, mostly iso-C_{28}. The yield of lube-base oil decreases gradually with increasing conversion as the yield of diesel fuel and gasoline increases. The major

product is diesel fuel at 99% conversion, only a 20% change in conversion. If the reaction is carried to 100% conversion, the major product becomes highly branched gasoline. Switching between these three fuels occurs at high conversion values. It appears possible to obtain the desired fuel range by adjusting the conversion at a selected temperature but maintaining relatively high conversion.

The fuel ranges contain more than 75% of branched isomers at all conversions. A highly branched isomer ratio results in a high octane number for gasoline and a low pour point for diesel and lube-base oil. The isomerization percentage increases slightly for gasoline and diesel fuel with increasing conversion, but this effect is negligible compared to the temperature effect.

Product distribution changes with increasing temperature (Figure 3). Temperatures are 220°C, 240°C and 250°C in Figure 3-a, b and c. All data are for 20 minute reactions with n-C_{28}. At 220°C, 79% conversion is reached while 100% conversion was attained at both 240°C and 250°C. The reaction at 240°C reached 100% conversion before 20 minutes and cracking increased. This effect can be seen in the product distribution for reaction at 250°C; 80% of the product is in the gasoline range with none in the lube-base range. The lube-base and most of the diesel fuel have already been cracked into gasoline. Low temperatures favor isomerization to branched alkanes.

Overall, temperature has a more significant effect on product distribution than time. The ability to vary time and temperature independently allows flexibility in the product. Moderate temperatures give rise to middle range products while lower temperatures favor heavier but branched products.

For this catalyst, hydroisomerization takes place first and then multibranched isomers begin to crack. Both catalyst properties and reaction conditions have an effect on the hydroisomerization and hydrocracking balance and product distribution. By adjusting reaction time and temperature it is possible to obtain high conversion to diesel fuel, gasoline or lube-base oil. Selectivity to branched isomers is high at high conversions with this catalyst.

Reactions with Zeolites
It is well known that zeolites, through their network of micropores, can show interesting properties by a molecular sieving effect and shape selectivity in adsorption and catalysis. Work has been started in this laboratory to study the use of various zeolites to control the nature of the products in the hydroisomerization and hydrocracking of hydrocarbons varying in chain length for C_{20} to C_{32}.

Three zeolite types, as powders, were obtained from Zeolyst International: two Y type zeolites with Si/Al ratios of 5:1 and 30:1, a mordenite (MOR) with a Si/Al ratio of 20 and a Beta type Zeolite with a Si/Al ratio of 25. Surface areas of these zeolites ranged from 925 m^2/gm for the Y type to 500 m^2/gm for mordenite. Since it is possible that the pores of these zeolites may be too small or too large, an amorphous silica-alumina sample was

obtained from Sasol; its Si/Al ratio was 40,

The aforementioned $Pt/ZrO_2/SO_4$ and $Pt/ZrO_2/WO_3$ catalysts can be used to convert long-chains, depending on conditions, to high cetane gasoline, diesel fuel and lube-base oils. Our aim with the zeolites is to obtain high yields of fractions in the diesel range with the remainder of the products as high octane gasoline. The first approach is to use the $Pt/ZrO_2/SO_4$ and $Pt/ZrO_2/WO_3$ catalysts in the presence of zeolites to direct product distribution to the desired products.

Several papers presented at the recent North American Catalyst Conference in Toronto in June, 2001 did indeed investigate the use of sulfated zirconia catalysts. One study used the zirconia-based catalysts supported on mesoporous silica, but this study was confined to the isomerization of n-butane. Another paper (Fang Li et al.) found that Pt/H-Beta modified by WO_xZrO_2 exhibited higher isomerization of n-heptane than Pt/H-Beta. Our work will deal with the hydroisomerization of F-T type waxy hydrocarbons to obtain diesel fractions.

Based on our early research, $Pt/ZrO_2/WO_3$ has been shown to be a very good catalyst for the hydroisomerization of long-chain (to C_{32}) normal alkanes. The use of hybrid Pt-promoted and amorphous-silica alumina shape selective supports is a possible way of combining the zirconia catalysts with zeolites having proper surface acidity and surface areas, to direct product distributions. The pore structure of the silica-alumina supports can be used to direct reaction selectivity.

Preliminary work was carried out on a Pt-Y zeolite (Pt-LZY82). At 230ºC, conversions and selectivities to the various fuel ranges are shown in Figure 4. When the Y zeolite was modified by the addition of Ca^{++} and reacted at 260ºC, the amount of the diesel fraction increased. This could be attributed to the lowering of acidity of the zeolite by addition of the Ca^{++}.
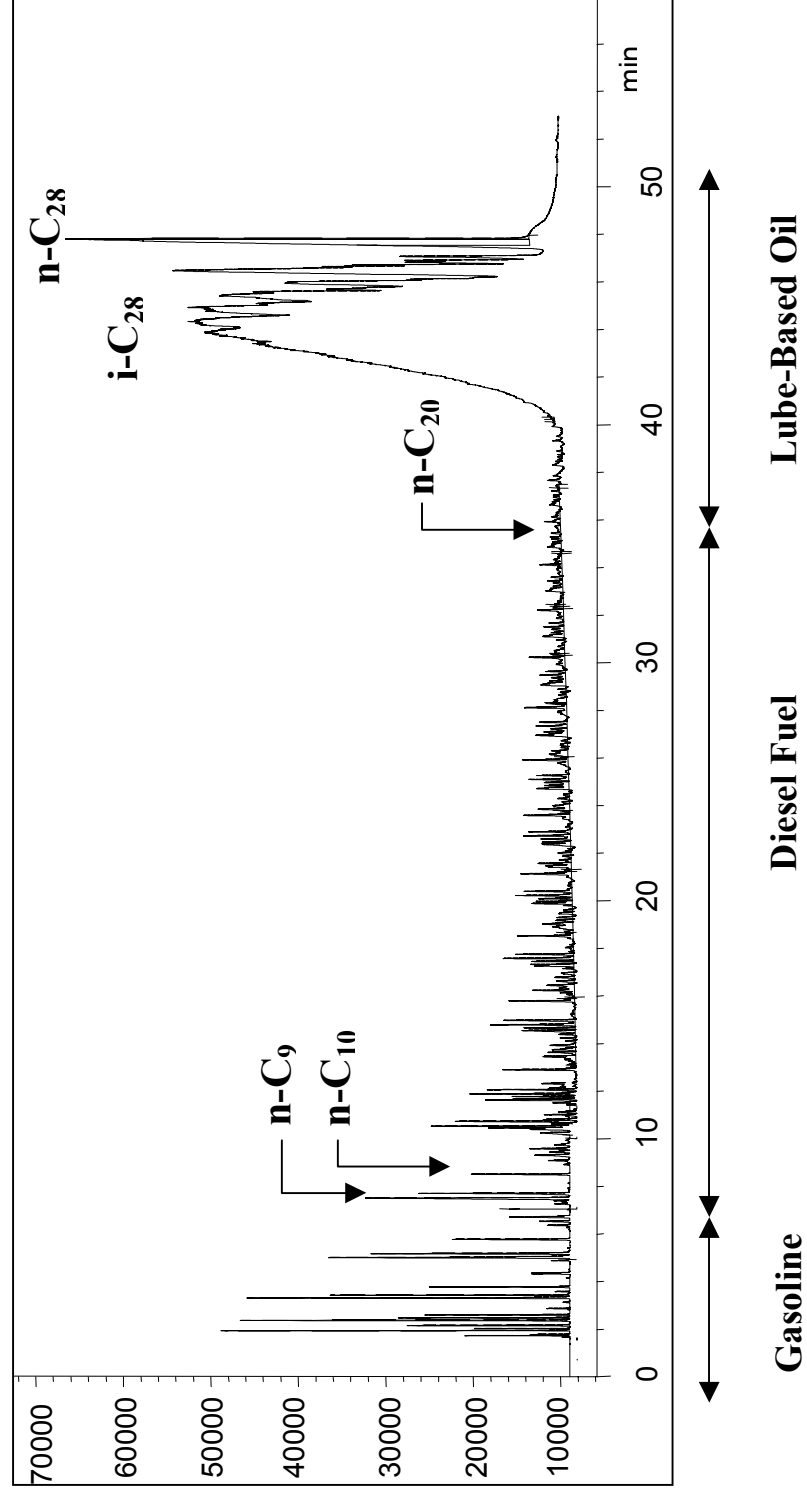
Figure 1 Typical GC Chromatogram for Reacted Octacosane (C_{28}) at $220°C$ and 500 psig
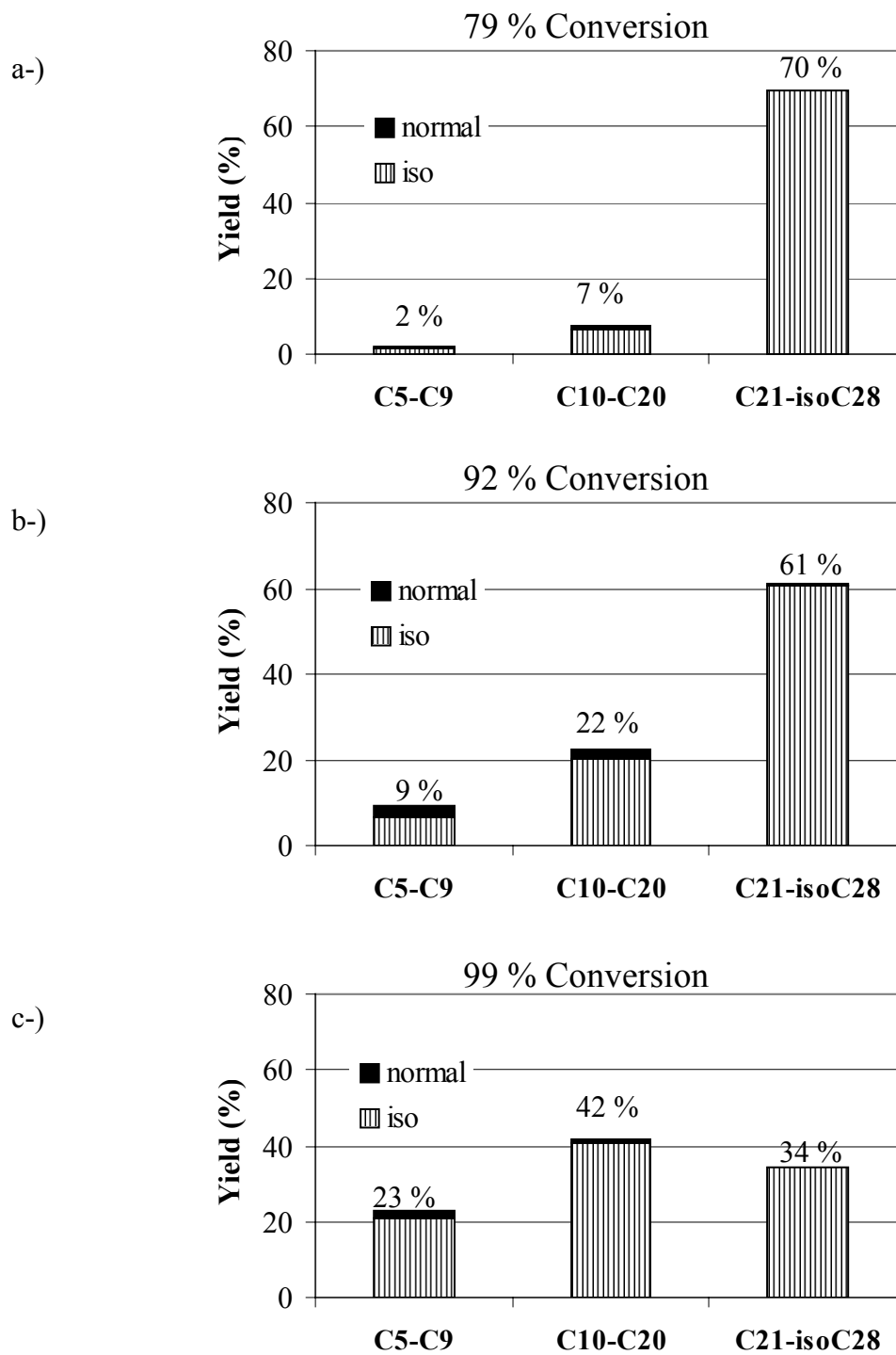
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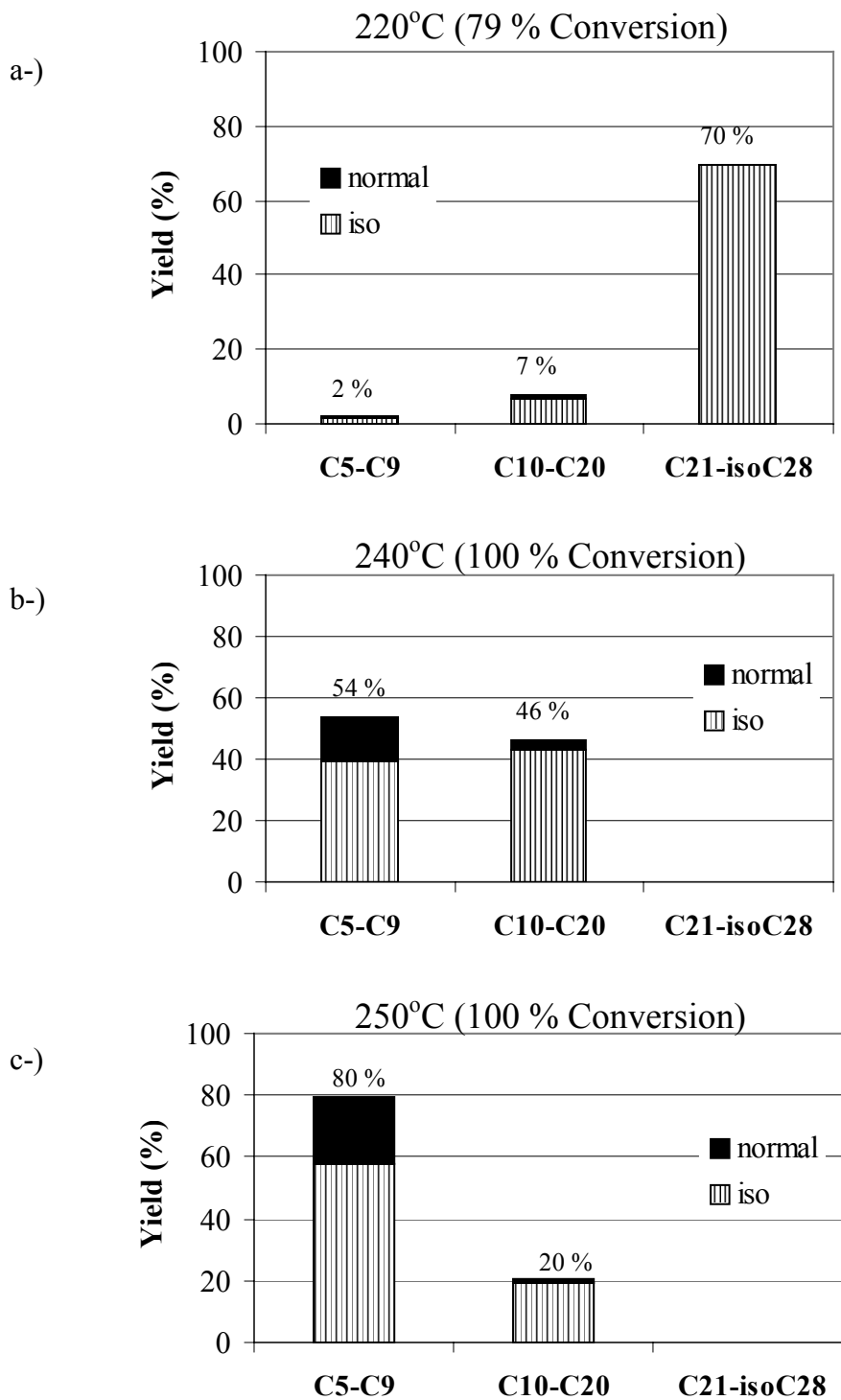Figure 2 Effect of Conversion on Product Distribution for Reacted C_{28} at $220^{o}C$ and 500psig

Figure 3 Effect of Temperature on Product Distribution of Reacted C_{28} at $220^{o}C$ and 500
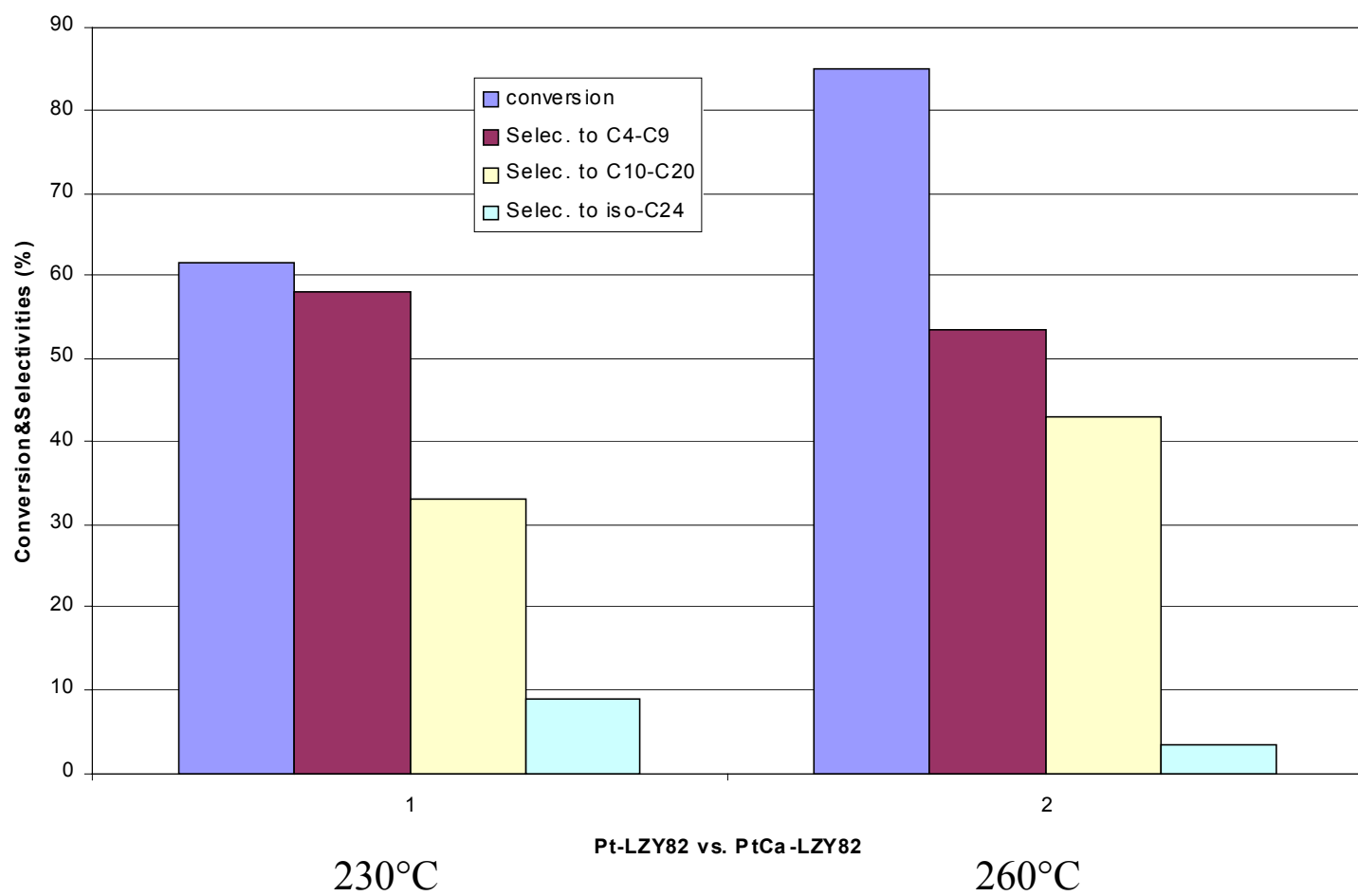
Figure 4. Conversion and selectivity for reaction of n-C$_{24}$ with Pt-Y(1) and PtCa-Y(2) zeolite catalysts.