

HIGH CONVERSION (98%) FOR THE HYDROGENATION OF 1-METHYLNAPHTHALENE TO METHYLDECALINS

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ABSTRACT

This work presents results from the hydrogenation of 1-methylnaphthalene. Aromatics are undesirable because of their toxicity, poor combustion characteristics and environmental impact. Saturated cyclic hydrocarbons with one or two rings show great promise for use in fuels. Methyldecalsins were used as feed in the second step of a two-stage operation for the production of high octane gasoline components from 1-methylnaphthalene, which represents coal derived liquids. Experiments were conducted in a stirred batch reactor with commercial as well as previously tested non-commercial catalysts under different reaction conditions. The data shows that a NiMo catalyst supported on titania-alumina produced high yields of methyldecalsins at 325°C and 1000 psi. The products were analyzed by GC/MS and ¹³C-NMR spectroscopy. The conversion to methyldecalsins were 98%. Previous methods yielded considerably lower conversion.

INTRODUCTION

It is widely agreed that the availability of petroleum in international trade is likely to diminish in the future. Research is being undertaken to develop economically competitive process for the conversion of coal, oil shale, tar sands and petroleum residues into liquid fuels. Although there has been significant advances both in improving the technology for converting coal to liquid fuels as well as in improving economics, the cost is still higher than for fuels produced from petroleum. Several of these coal liquefaction processes rely on the use of a catalyst.

Coal liquefaction processes generally involve a number of mechanical and chemical steps. Catalytic hydrogenation and cracking of the coal liquids take very important place in the development of coal liquefaction technology. The catalyst is believed to bring about the conversion of various species to molecules which are capable of cracking or depolymerizing coal particles by hydrogen transfer.

Coal liquids are very complex mixtures, mostly containing ring-type molecules, both aromatics and hydroaromatics, with various types of functional groups attached. 1-Methylnaphthalene (1-MeNAPH) was selected as a model compound representing coal-derived liquids. The immediate objective of this part of the project is to convert 1-MeNAPH to methyldecalsins. Methyldecalsins were in this study used as feed in the second stage of a two-stage operation for the production of high octane gasoline components from 1-MeNAPH, but they can also be used directly as a component in jet fuels.¹⁻⁶

EXPERIMENTAL

Catalyst Preparation. NiMo/TiO₂-Al₂O₃ and NiMo/SiO₂-Al₂O₃ catalysts were prepared by incipient impregnation method. The support TiO₂-Al₂O₃ or SiO₂-Al₂O₃ was calcined in air at 540°C for 16 h, ground and sieved to -100 mesh. All prepared catalysts contained 25 mmol of Ni and 77 mmol of Mo per 100 g of support. A weighed sample was first impregnated with an aqueous solution of ammonium molybdate ((NH₄)₆Mo₇O₂₄·4H₂O, Alfa Product). The impregnated sample was oven-dried at 120°C for 16 h and then impregnated with a salt solution of nickel nitrate (Ni(NiO₃)₂·6H₂O, Fischer Scientific Co.).

NiW/TiO₂-Al₂O₃ and NiW/Al₂O₃ was impregnated in a single step with an aqueous solution containing calculated amounts of ammonium meta tungstate((NH₄)₆H₂W₁₂O₄₀·3H₂O, Cerac inc.) and nickelous nitrate followed by drying at 120°C for 16 h. The resulting material contained 88.9 mmol of Ni and 165.6 mmol of W per 100 g of TiO₂-Al₂O₃ or 100 g of Al₂O₃. Each catalyst was finally calcined in air at 540°C for 16 h.

NiW/SiO₂-Al₂O₃ (Harshaw Catalysts), Pt/REX and Pd/REX (proprietary) are commercial catalysts used for the experiments.

Resulfidation. All catalysts except Pt/REX and Pd/REX were sulfided in a tubular reactor prior to use. Nitrogen with a flow rate of 60 ml/min purged the sulfidation reactor to remove the air. The catalyst was heated to 400°C under nitrogen flow and kept at this temperature and inert conditions for an hour. The gas flow after this desorption step was changed to 10% (by wt) hydrogen sulfide in hydrogen. The reactor was maintained at 400°C at the same flow rate for 2 h. Subsequently, it was purged with nitrogen at the same conditions for an hour to remove the residual amount of hydrogen sulfide and then cooled to ambient temperature.

Reaction Experiments. Reaction experiments were conducted in a 300 cc batch reactor equipped with a magnetic drive stirrer, heating assembly, gas inlet and gas collector. Weighed amount of 1-MeNAPH (Aldrich Chemicals, 98%) and the sulfided catalyst in a feed to catalyst ratio of 10 to 1 were quickly dumped into the reactor. The sealed reactor was repeatedly purged with nitrogen and subsequently hydrogen to replace the air, and then pressurized with hydrogen and heated to a reaction temperature over about 20 minutes at slow stirring rate (80 rpm). Once the desired temperature was reached, the stirring speed was increased to 800 rpm and the reactor was remained at reaction temperatures for 1-10 h. Sulfided fresh catalyst was added to reaction mixture after first 5 h.

Product Analysis. Liquid products were identified by GC and GC/MS (Hewlett Packard 5890 Series II GC with a HP 5971 Mass Selective Detector). DB-5 column (30mx0.25mm i.d.x1.0µm, J&W Scientific) with a temperature program from 40 to 260°C. Gas products were analyzed by a Shimadzu GC-14A gas chromatograph, equipped with a flame ionization detector (FID) and Chromosorb 102 80/100 column (6'x1/8"x0.0085", Supelco). The column temperature ranged from 40 to 200°C. Scotty standard gases were used for calibration.

Methyldecalins from the hydrogenation of 1-MeNAPH were also identified by ¹³C-NMR spectroscopy (VXR-400).

RESULTS AND DISCUSSION

Initial experiments were performed at 325°C and 1000 psi for 10 h with a feed to catalyst ratio of 10 to 1 by weight. The results are given in Figure 1. All conditions remained the same for all experiments, changing only the catalyst. The total conversion was defined as

$$\% \text{Total Conversion} = 100 \times \frac{\text{Feed} - \text{Feed in product}}{\text{Feed}}$$

Liquids were weighed just after completion of the reaction, and gas amounts were calculated from gas chromatograms. Liquid product distribution was calculated based on converted material. The products can be subdivided into four different groups.

- (1) Cycloalkanes (*methyldecalins*, *cyclohexanes* and *cyclopentanes* which are mostly alkyl substituted and 'other cycloalkanes' which include decalins, octahydroindenes, bicycloheptanes, etc.)
- (2) Alkanes (*normal* and *branched*)
- (3) Alkenes and cycloalkenes
- (4) Aromatics (*Methyltetralins*, and 'other aromatics' which include bigger than one ring aromatics)

Near 100% conversion was achieved with each catalyst but product distribution i.e. the depth of ring hydrogenation varies widely (Figure 1). NiMo/TiO₂-Al₂O₃ exhibited by far the highest hydrogenation activity followed by NiW/Al₂O₃ and NiW/TiO₂-Al₂O₃. Pt/REX and Pd/REX exhibited high cracking activity with a product dominated by aromatics. NiW/SiO₂-Al₂O₃ gave a mixture of hydrogenation and cracking products. Conclusively, the most effective catalyst in hydrogenation of 1-MeNAPH is NiMo/TiO₂-Al₂O₃ catalyst with a 97.2% conversion to methyldecalins at 325°C and 1000 psi.

Figure 2 shows the effect of temperature on the yield and distribution of liquid products from 1-MeNAPH using NiMo/TiO₂-Al₂O₃. The total conversion slightly decreased when the temperature was increased from 350°C to 450°C. The yield of methyltetralins and methyldecalins also showed a reverse temperature dependence. Conversion to one ring compounds, given under 'other aromatics', was observed as a result of cleavage reactions of tetralins at high temperatures.

Since reactions at higher temperatures result in cracking, the temperature was decreased to 325°C using NiMo/TiO₂-Al₂O₃ catalyst. Figure 3 summarizes the results under different reaction conditions, keeping only the temperature constant at 325°C. A total conversion of 100% was achieved, and the yields of methyldecalins were over 92% for each experiment. The yield of

methyldecalins only changed from 97.2 % to 98.6% as pressure was increased from 1000 psi to 1500 psi. When only the feed/catalyst ratio was changed from 10/1 to 5/1 at 1000 psi for 10 h reaction time, the conversion to methyldecalins reached to 99.5%,

Mass balances were closed with 4 to 13% error. The amount of gas products was 0.1-8.4% depending on reaction conditions. The gaseous fractions analyzed by GC were predominantly composed of methane at 325°C with NiMo/TiO₂-Al₂O₃, NiW/TiO₂-Al₂O₃ and NiW/Al₂O₃ catalysts because these catalysts have higher hydrogenation activities compared to NiW/SiO₂-Al₂O₃, Pt/REX and Pd/REX catalysts. The latter exhibited higher yields of C₃-C₄ hydrocarbons. The temperature effect on the distribution of gas products from hydrogenation of 1-MeNAPH at 350-450°C with NiMo/TiO₂-Al₂O₃ catalyst showed that the yields of C₁-C₂ hydrocarbons increased with temperature whereas those of C₃-C₄ hydrocarbons decreased.

Verification of Methyldecalin Synthesis. Primary identification of methyldecalins, separated by gas chromatography, was done by mass spectrometry and comparisons with database cracking patterns.⁷ The results from GC/MS are given in Figure 4. Secondary identification was given by matching retention times with published boiling points. Figure 5 compares the present results with those of Weitkamp et al.^{7,9} Filled circles represent retention times for eight isomers as measured in the present work and by Weitkamp et al. Open circles represent two more isomers identified as methyldecalins by mass spectrometry in the present study and extrapolated values in Weitkamp's work. Additional support for the identification of these compounds as 9-methyldecalins was given by boiling points. Finally, consistency between different spectra was verified by comparisons with a compiled list of retention times for all identified compounds within the present project. Some uncertainties still persist for the distinction between different isomers except in the case of methyldecalins, where full agreement exists with literature.^{7, 8, 10-12}

Figure 6 shows the ¹³C-NMR spectrum of the product from hydrogenation of 1-MeNAPH. The signals were integrated into two groups: (a) aliphatic carbons; chemical shift, δ=15-55 ppm, and (b) aromatic carbons; δ=125-160 ppm. It was observed that the aromaticity was about 2% and that the isomers have eleven carbon atoms in different proportions.

CONCLUSION

High conversions of methyldecalins (up to 99.5%) were obtained from the hydrogenation of 1-MeNAPH using NiMo/TiO₂-Al₂O₃ catalyst at 325°C and 1000 psi for 10 h reaction time. The hydrogenation processes consist of a complex array of kinetic steps involving a series of intermediates producing methyldecalins simultaneously. The intermediate products are mixtures of methylnaphthalenes, methyltetralins and methyldecalins.

When reaction temperatures were increased, hydrocracking reactions set in as observed in Figure 4.3. The results from the present study agree with the work of Weitkamp et al.^{7, 8, 13} They studied the hydrogenation of alkylnaphthalenes using a broad variety of catalysts. With most catalysts, yields of methyldecalins up to 90% range were obtained from individual methylnaphthalenes after 30-40 h reaction time over Pt(0.6%)/Al₂O₃ catalyst at 200°C.

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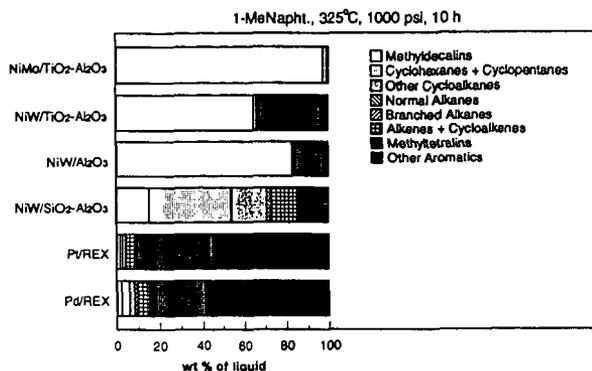


Figure 1. Yield and distribution of liquid products from hydrogenation/hydrocracking of 1-MeNAPH using different catalysts. Difference to 100% is the unconverted material. Feed/catalyst ratio is 10/1.

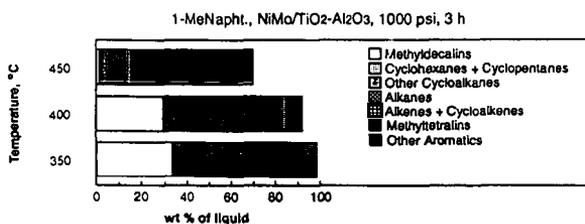


Figure 2. Effect of temperature on the yield and distribution of liquid products from hydrogenation/hydrocracking of 1-MeNAPH. Difference to 100% is the unconverted material. Feed/catalyst ratio is 10/1

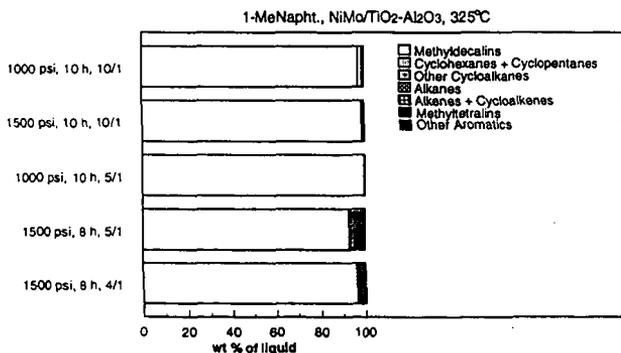


Figure 3. Effect of variable combinations on the yield and the distribution of liquid products from the hydrogenation of 1-MeNAPH using NiMo/TiO₂-Al₂O₃ catalyst. 10/1, 5/1 and 4/1 define feed to catalyst ratios.

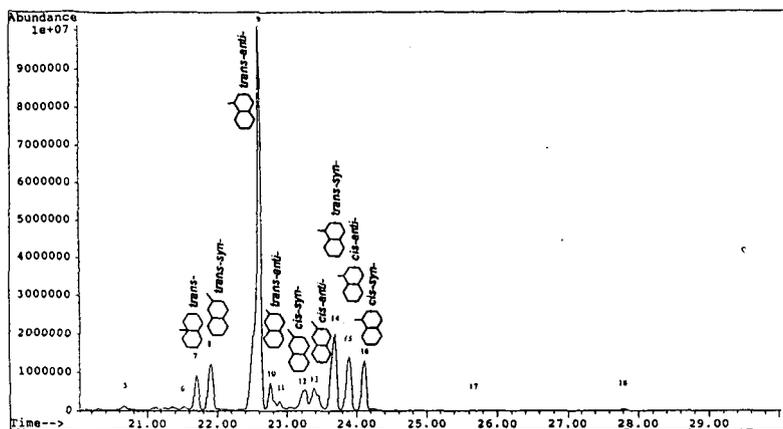


Figure 4. Identification of methyldecalin by GC/MS.

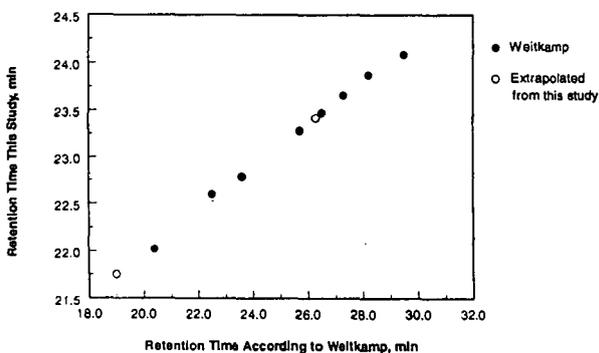


Figure 5. Identification of isomers of methyldecalin by comparison with published GC retention times.

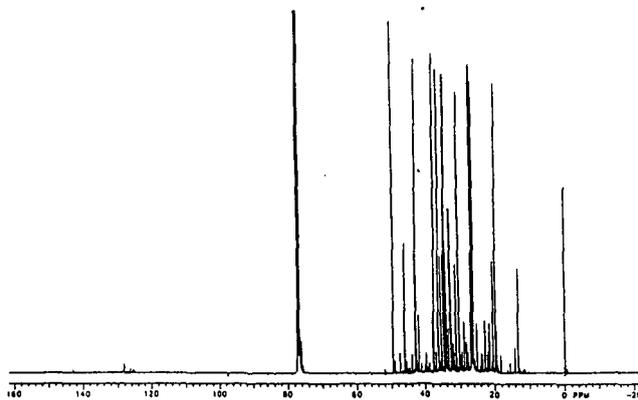


Figure 6. ^{13}C -NMR spectrum of the product from hydrogenation of 1-MeNAPH.