

CONVERSION OF FATTY ACIDS AND ESTERS TO LOW-AROMATIC GASOLINE

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ABSTRACT

Agricultural oils and by-products have been used as fuels, but they can also serve as precursors for producing transportation fuels that require a highly isoparaaffinic composition for high performance. Hydrocracking and reforming of biomass materials to the isoparaaffinic composition desired for gasoline are reported in this paper. Several catalysts, including natural and synthetic clays, have been effective for conversion of fatty acids and triglycerides to high-quality gasoline products. Reactions with nickel-substituted synthetic mica montmorillonite gave high yields of distillate in the gasoline range. A high percentage of the product was isoparaaffinic or branched alkanes (55%–61%) and a low percentage was aromatic. Rapeseed oil was converted to a highly isoparaaffinic product with minimal formation of benzene or toluene. These product compositions are appropriate for transportation fuels with low environmental risks.

INTRODUCTION

Fuels derived from renewable resources currently comprise only a small proportion of the total fuel utilized in the U.S. Renewable biomass-derived fuels recycle carbon so that fuel combustion does not contribute to the accumulation of carbon dioxide in the atmosphere. Other advantages are the consistency of the energy supply in U.S. and even regional markets. Further development of liquid fuels for use in high-performance engines from renewable energy resources is needed. In order to be environmentally acceptable, the transportation fuels must contain very low amounts of benzene and other aromatic components. Catalytic methods are needed for converting crop oils to a low-aromatic fuel. The use of waste oils from vegetable oil processing or cooking and tall acids from paper pulping has the potential for producing a low-cost fuel.

The conversion of tall and vegetable oils to alternative fuels with zeolite catalysts resulted in products containing very high concentrations of aromatic components (1–6). The objective of our investigations is to evaluate the catalytic conversion of oils and fatty acids to highly aliphatic gasoline-range products. Therefore, we have investigated catalysts and conditions that minimize the formation of aromatics and conserve the high hydrogen content of the fatty raw materials.

Synthetic clays, such as nickel-substituted synthetic mica montmorillonite (NiSMM), were effective for cleaving carbon–carbon bonds and isomerizing the alkyl chains to give branched alkanes, without extensive formation of aromatic hydrocarbons (7–9). Reactions of fatty acids and oils with NiSMM catalyst is reported in this paper.

EXPERIMENTAL

Catalytic Hydrotreating Reactions. Preparation and characterization of NiSMM was reported elsewhere (7–9). In a typical run, 0.5 g of the rapeseed oil or oleic acid and 0.25 g of the catalyst were placed in a 12-mL microreactor. The microreactor was evacuated, pressurized with 1000 psi (6.9 MPa) of hydrogen (corresponding to 28 mmol), and placed in a rocking autoclave heated to the desired temperature. The gas pressure increased from heating the gas (2400 psi at 400°C) and then increased further, owing to decarboxylation and other gas formation reactions. The heating was continued for 1–3 hours. At the end of the reaction period, the microreactor was cooled to room temperature, degassed, and opened. The desired amount of the internal standard was added to the product slurry, and the product slurry was transferred into a centrifugation tube by washing with methylene chloride and the solid catalyst removed by centrifugation.

Analytical procedures: instrumentation. Identification of the product components in the gasoline range was by retention time measurement on a Petrocol 100-m capillary gas chromatograph (GC) column and by gas chromatography/mass spectrometry (GC/MS) analysis using a Finnigan 800 ITD ion trap detector with a HP 5890A gas chromatograph and a J&W 30-m x 0.32-mm (ID), 1.0-micron DB-5 film.

Quantitative GC/FID analyses were performed with a Hewlett Packard 5880A gas chromatograph equipped with a Petrocol 100-m capillary column. Since it was not found in significant amounts in the reaction products, octadecane was added as the internal standard. Amounts of aromatic components were determined by multipoint calibration of the system with standard mixtures. Alkane components were determined from the area percent ratio with respect to octadecane, assuming the same response factor. To calculate the product molecular size distribution, the quantities of components in two size groups, C_4 – C_9 and C_{10} – C_{17} , were added, and are reported as a percentage of the total volatile liquid

product. Quantities of components in the compound type groups, such as n-alkanes, branched and cyclic alkanes, and aromatics, were also added and reported as percentages of the light volatile fraction that includes C_4 - C_{17} components.

GC analyses for higher molecular weight volatiles were obtained using a Quadrex 15-m by 0.25-mm diameter aluminum-clad capillary column with a 0.10- μ m methyl 5% silicone phase with 1.0-ml/min H_2 carrier measured at 400°C and on-column injection. Octadecane was added as the internal standard. Amounts of compounds in the range C_{18} - C_{70} were determined from the area percent with respect to octadecane and are reported as a percentage of the total volatile product. Total volatile yields were determined by adding the quantities in the three ranges or fractions described above. These are reported as weight percent yield of oleic acid starting material.

RESULTS

Catalytic hydrocracking/hydroisomerization reactions were conducted with a crop oil and a by-product oil to evaluate the potential for synthetic clay catalyst upgrading to environmentally acceptable transportation fuels that contain large amounts of branched alkanes (isoparaffins) and low amounts of aromatics. The crop oil was inexpensive rapeseed oil, a triglyceride that contains large amounts of inedible erucic acid. The paper pulping by-product, tall oil, is composed of several fatty acids (mainly oleic and linoleic acids), resin acids, and sterols. Oleic (9-octadecenoic) acid was used as a model substrate in preliminary studies to determine appropriate conditions for the tests. Two synthetic clay catalysts were used in the reactions. In all the tests, the conversion of the oleic acid to liquid and gas products was 100%, and no coke or insoluble materials were detected on the recovered catalyst.

Noncatalytic Reaction. The noncatalytic reaction of oleic acid was performed to determine the nature of the products and yields for the thermal reactions of fatty materials at 400°C under hydrogen atmosphere. Only a minor portion (26 wt%) of the products consisted of volatile liquids. Analyses showed the presence of large amounts of alkanes higher than C_{18} (63% of the volatile liquid material). Very small amounts of gasoline-range components (9% of volatile liquid) were produced. The high molecular weight compounds are dimers and other oligomers that are normally found in fatty acid pyrolysis products. Other alkane products resulted from secondary cracking reactions of the oligomeric materials, but very few branched alkanes were formed. The majority of product from the uncatalyzed reaction was nonvolatile polymeric material, since it did not appear in the GC analyses. Thus, the noncatalytic thermal hydropyrolysis of oleic acid at moderate temperature does not effectively produce a usable fuel for a high-performance engine.

Reactions with NiSMM Catalyst. The NiSMM-catalyzed hydrocracking reaction of oleic acid was carried out under several conditions to determine the effects of temperature, hydrogen pressure, and reaction time for production of low-aromaticity gasoline. The reaction products were a complex mixture of hundreds of components formed as a result of the extensive rearrangements or isomerizations of the primary cracked or oligomeric products. The major products from the synthetic-clay-catalyzed reactions were the desired isoparaffins: mono-, di- and trimethylalkanes.

The reaction of oleic acid with NiSMM at 400°C for 1 hour with 2400-psi-hydrogen pressure gave a high yield (80 wt%) of volatile liquid products. A large percentage of the product (69%) was in the gasoline range. High-resolution GC analysis indicated that the gasoline-range materials were composed mainly of branched alkanes and cycloalkanes (78%), with lower amounts (8%) of n-alkanes. Small amounts of aromatics were present, with only 8% BTEX in the liquid product.

The reaction period for oleic acid with NiSMM catalyst was extended to 3 hours to determine if the longer time would give higher yields of liquids in the gasoline range. The reaction for the 3-hour period also gave a high yield of liquid product (76%), but the distribution with respect to molecular size was similar to the reaction carried out for 1 hour (72% in the gasoline range). More importantly, the composition of the gasoline-range product was more aromatic than that from the 1-hour reaction, with 20% BTEX present. Thus, the longer reaction time period resulted in a less desirable product because of the higher aromatic content.

The reaction of oleic acid with the NiSMM catalyst at a lower temperature might be expected to give a less aromatic product. At 350°C for 3 hours with 2200-psi-hydrogen pressure the reaction gave 76% conversion to volatile product. Low aromatic content was obtained (9% BTEX), but a lower percentage of the volatile liquid product (56%) was in the gasoline range. Despite the lower yields at this lower temperature, the NiSMM catalyst exhibits good selectivity for the hydrocracking and hydroisomerization reaction of the aliphatic chains.

Rapeseed Oil Reaction. Rapeseed oil was reacted with the NiSMM catalyst at 400°C for 1 hour with 2240-psi-hydrogen pressure. The conversion to volatile liquid was a little lower than that obtained with oleic acid (58%). High molecular weight ($> C_{12}$) material was absent, indicating that fewer dimerization or condensation reactions occurred with the triglyceride oil than with the free oleic acid. A higher yield of gas product was obtained with the rapeseed oil, compared to the oleic acid. A possible explanation for these yield results is that the catalyst remained more active in the rapeseed oil reaction.

The composition of the product from rapeseed oil was much more isoparaﬀinic than that obtained from the oleic acid. Only 4% n-alkanes were present, and branched alkanes comprised most of the product (90%). The aromatic content was very small, BTEX accounted for only 6% of the liquid product, and the benzene concentration was only 0.7%.

CONCLUSION

Conversion of biomass fuels containing fatty acids to a highly calorific and environmentally acceptable fuel can be effected by catalytic processing. In the NiSMM-catalyzed reactions described in this paper, the aliphatic nature and inherent large hydrogen content of vegetable oils is mostly preserved, and the structures were mostly isomerized to isoparaﬀinic molecules. Thus, not only was a high-performance fuel produced, but also one with low benzene content and consequently low toxicity. Previous investigations of vegetable oil conversions to fuels with shape-selective zeolite (HZSM-5) catalyst gave liquids that were highly aromatic (60%–70% aromatic content). Yields were similar to those reported here.

Coaddition of steam and tetralin could improve the conversion substantially at moderate temperatures (3–5). Steam addition also improved catalyst life and produced less coking.

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