

DEPOLYMERIZATION-LIQUEFACTION OF PLASTICS AND RUBBERS. 1. POLYETHYLENE, POLYPROPYLENE AND POLYBUTADIENE.

Xin Xiao, Włodzimierz Zmierczak and Joseph Shabtai
Department of Chemical and Fuels Engineering
University of Utah
Salt Lake City, Utah 84112

ABSTRACT

Processing conditions were developed for high-yield depolymerization-liquefaction of isotactic polypropylene (M.W., ~250,000) into a light, gasoline-like product. At 380-420 °C, an initial H₂ pressure of 1200 psig, with 1 wt% of finely dispersed Fe₂O₃/SO₄²⁻ or ZrO₂/SO₄²⁻ as solid superacid catalysts, the polypropylene is converted (yields, 72-83 wt%) into a liquid product consisting predominantly of C₅-C₁₂ branched paraffins. The change in product composition as a function of reaction temperature, time, and catalyst concentration, was examined and optimal conditions for production of gasoline-range branched paraffins determined. Depolymerization-liquefaction of polyethylene with the same catalysts required higher processing temperature (420-450 °C) and longer reaction time. Liquid yields in the range of 78-85 wt% were obtained and the product consisted of a mixture of C₅-C₃₀ (mostly C₅-C₁₂) normal paraffins, accompanied by some branched isomers. Polybutadiene (98 wt% *cis*) was depolymerized-liquefied at 400 °C and 1200 psig initial H₂ pressure in ~85 wt% liquid yield. The product consisted of a mixture of paraffins and cyclic compounds, including alkylcyclohexanes, alkylcyclopentanes, and alkylbenzenes with C₁-C₃ alkyl groups.

Keywords: depolymerization, liquefaction, plastics

INTRODUCTION

The effective disposal of waste industrial polymers is now recognized to be a major environmental problem in North America. Plastics and rubbers are troublesome components for landfilling, inasmuch as they are not presently biodegradable. Their destruction by incineration poses serious air pollution problems due to the release of airborne particles and carbon dioxide into the atmosphere. An alternative would be true recycling, i.e., conversion into monomers that can be reused. However, polyethylene and polypropylene do not depolymerize thermally to ethylene or propylene with sufficient selectivity. On the other hand, waste plastics and rubbers can be regarded as a potentially cheap and abundant source for fuels. Thermodegradation of polyolefins has been investigated extensively since World War II¹⁻⁵, but relatively few studies on the catalytic conversion of the polymers have been carried out, especially for production of liquid fuels. Recently there have been reports on the pyrolysis of polyolefins to aromatic hydrocarbons with activated carbon-supported metal catalysts^{6,7}; cracking of polystyrene and polyethylene on silica-alumna⁸; and reforming of heavy oil from waste plastics using zeolite catalysts⁹. Most of these catalytic studies were conducted under nitrogen at ambient or low pressure. The present paper is concerned with an investigation of the catalytic depolymerization-liquefaction behavior of three representative commercial polymers, i.e., polypropylene, polyethylene and polybutadiene using superacid catalysts¹⁰⁻¹⁶ under high H₂ pressure. The objective was to determine suitable conditions for conversion of such polymers into light liquid fuels, as well as to obtain data needed for predictive modeling of waste polymers coprocessing with coal.

EXPERIMENTAL

Materials. High density polyethylene (d, 0.959 g/cm³; M.W., 125,000) and isotactic polypropylene (d, 0.900 g/cm³; M.W., 250,000) were obtained from Aldrich Chemical Company; and polybutadiene (98% *cis*; d, 0.910 g/cm³; M.W., 197,000) from Scientific Polymers Products, Inc.

Catalysts. Three types of solid superacid catalysts, i.e., Fe₂O₃/SO₄²⁻, ZrO₂/SO₄²⁻ and Al₂O₃/SO₄²⁻ were synthesized. The preparation of the first two was the same as recently described in detail elsewhere¹⁶. Al₂O₃/SO₄²⁻ was prepared by the following procedure: 12.4 g of Al₂(SO₄)₃·(14-18)H₂O was dissolved in 44 ml of distilled water and subjected to hydrolysis at room temperature by slowly adding 28-30% NH₄OH with vigorous mixing, until pH = 8.5 was reached. The precipitate was filtered, washed with distilled water, and then dried at 110 °C for 2 h. The dry solid was pulverized and calcined at 550 °C for 2 h. The resultant Al₂O₃, 2.0 g, was treated with 50 ml of an aqueous solution with concentrations of 1.5M (NH₄)₂SO₄ and 1.0 M H₂SO₄ for 1 h with continuous stirring, then filtered, washed with ~100 ml of water, dried at 110 °C for 2 h, and calcined at 600 °C for 3 h.

Experimental Procedure. A mixture of the polymer, 10.0 g, and catalyst, 0.1 or 0.2 g (without any solvent), was introduced in a 50 ml Microclave reactor (Autoclave Engineers). The latter was closed, purged with nitrogen, and then pressurized with hydrogen to a selected initial pressure. The reactor was heated to the desired temperature in 12-15 min, and stirring (500 rpm) was started after reaching the melting or softening point of the polymer (130-189°C). Initial H₂ pressures from ambient to 2000 psig resulted in reaction pressures between 350-3600 psig in the reaction temperature range of 380-465 °C.

Analytical Methods. At the end of each experiment, the reactor was cooled down and the gas product was passed through a stainless steel trap kept at liquid nitrogen temperature. After weighing, the condensed gas was analyzed by GC. It consisted mostly of C₁-C₄ components, accompanied by some C₅, C₆, and traces of C₇, C₈ compounds. In runs with partial conversion, the liquid and solid products were removed from the reactor and weighed. The liquid was separated by decantation and filtration. The solid was rinsed with a little of n-hexane, dried, and weighed. The solid was then washed with n-hexadecane (~80 °C) and n-hexane (room temperature), dried and weighed in order to determine the weight of recovered catalyst. In this way, the product was separated and the weight of gas, liquid, solid and recovered catalyst was determined. The mass balance of the runs was 90-95% (relative to the weight of the feed). Gas and liquid products were identified mainly by GC, GC/MS and FTIR, and quantitatively analyzed by gas chromatography and simulated distillation (SIMD). Columns used for gas products: 4 m x 0.3 cm o.d. stainless steel packed with Chromosorb 102; for liquid products: 4 m x 0.3 cm o.d. stainless steel packed with 10% OV-17 on Chromosorb W-HP; for SIMD: 0.5 m x 0.3 cm o.d. stainless steel, Supelco PETROCOL™ B column.

RESULTS AND DISCUSSIONS

1. Polypropylene. At 390 - 420 °C and an initial H₂ pressure of 1500 psig, with 1.0 wt% of ZrO₂/SO₄²⁻ as catalyst, and a reaction time of 2.0 hours, the polypropylene was converted in very high yield (over 90 wt%) into a low-boiling liquid product. Branched C₅-C₁₀ paraffins (and some olefins) were predominant components of the product. Results on the change in product composition as a function of reaction temperature are given in Figure 1. As seen, the gasoline range fraction (C₅-C₁₂) reached a maximum (~64.5 wt%) at 400-410 °C, then decreased slowly at higher temperature. The C₁₃₊ components decreased and the C₁-C₄ gas increased with increase in temperature. At 400 °C, about 64 wt% of gasoline range, 29 wt% of higher hydrocarbons and 7 wt% of gas are produced. The depolymerization-liquefaction of polypropylene was investigated also as a function of reaction time. The change in product composition showed the same trends as those indicated above for the temperature effect. This demonstrated the potential of a controllable stepwise depolymerization of polypropylene into light liquid hydrocarbons. The H₂ pressure effect was smaller compared with those of reaction temperature and time. Increase in H₂ pressure from 15 to 500-1500 psig suppressed gas formation, decreased the amount of C₁₃₊ products, and increased gasoline boiling range production. A comparative study of the three different types of solid superacid, i.e., Fe₂O₃/SO₄²⁻, ZrO₂/SO₄²⁻ and Al₂O₃/SO₄²⁻ (see Experimental) was also performed, keeping other processing variables constant (reaction temperature, 410 °C, time 1.0 h, initial H₂ pressure 1500 psig, catalyst amount, 1.0 wt%). For comparison, a run without catalyst was also carried out. The extent of depolymerization of the feed into gasoline range hydrocarbons was significantly higher in the catalytic runs as compared with that in the thermal (non-catalytic) run. Among the catalysts examined, the order of depolymerization activity was Al₂O₃/SO₄²⁻ > ZrO₂/SO₄²⁻ > Fe₂O₃/SO₄²⁻. Based on the change in product composition as a function of reaction temperature and reaction time, a plausible carbonium ion mechanism for depolymerization of polypropylene can be considered (see Figure 4).

2. Polyethylene. Liquid yields in the range of 76-87 wt% were found for polyethylene with ZrO₂/SO₄²⁻ as catalyst at reaction temperatures in the range of 420-450 °C. The product consisted of a mixture of C₅ -C₃₀ (mostly C₅-C₁₂) normal paraffins and smaller amounts of branched isomers. Results on the change in product composition as a function of reaction temperature are given in Figure 2. The gasoline range fraction increased to a maximum of 63 wt% at 450 °C and then decreased at 465 °C. The C₁₃₊ components decreased while C₁-C₄ gas increased with increase in reaction temperature. The change in product composition as a function of reaction time (between 0.5-3.0 h) showed trends similar to those of the temperature effect. This was in good agreement with the above results for polypropylene and again demonstrated the controllable stepwise break-down of the polymer. The effect of H₂ pressure (500-2000 psig) on the product composition was relatively weak. As the H₂ pressure was increased from 500 to 1500 psig, the gasoline boiling range fraction increased while the C₁₃₊ fraction decreased. However, for H₂ pressures higher than 1500 psig, the concentrations of gasoline range and C₁₃₊ fractions remained relatively stable.

3. Polybutadiene. Polybutadiene was smoothly depolymerized-liquefied at 400 °C and 1200 psig initial H₂ pressure, with 1 wt% of Fe₂O₃/SO₄²⁻ as catalyst. The liquid yield was about 85 wt%. Figure 3 shows the GC/MS of the gasoline boiling range product. As seen, the product consists of a mixture of paraffins and cyclic compounds, including alkylcyclohexanes, alkylcyclopentanes, and alkylbenzenes with C₁-C₃ alkyl groups (C₁-C₃ indicating either single or two alkyl substituents). The formation of cyclic hydrocarbons from polybutadiene can be explained as follows. Butadiene obtained by depolymerization of polybutadiene, can undergo fast cyclodimerization to form 4-vinylcyclohexene, which undergoes a sequence of rearrangement and aromatization (or ring hydrogenation) reactions to yield a full range of alkylsubstituted naphthenes and benzenes¹⁷.

CONCLUSIONS

It is found that representative polyolefins, e.g., polypropylene, polyethylene and polybutadiene, undergo high-yield depolymerization-liquefaction in the temperature range of 380-450 °C, under H₂ pressures of 1200-2000 psig, and in the presence of catalytic amounts of finely dispersed solid superacids, i.e., Al₂O₃/SO₄²⁻, ZrO₂/SO₄²⁻ or Fe₂O₃/SO₄²⁻. The depolymerization-liquefaction process is easily controllable for preferential formation of gasoline-range hydrocarbons. Production of the latter can be rationalized in terms of stepwise breakdown of the polymeric chains by a carbonium ion mechanism. The data obtained can be used for predictive modeling of coal coprocessing with waste polymers.

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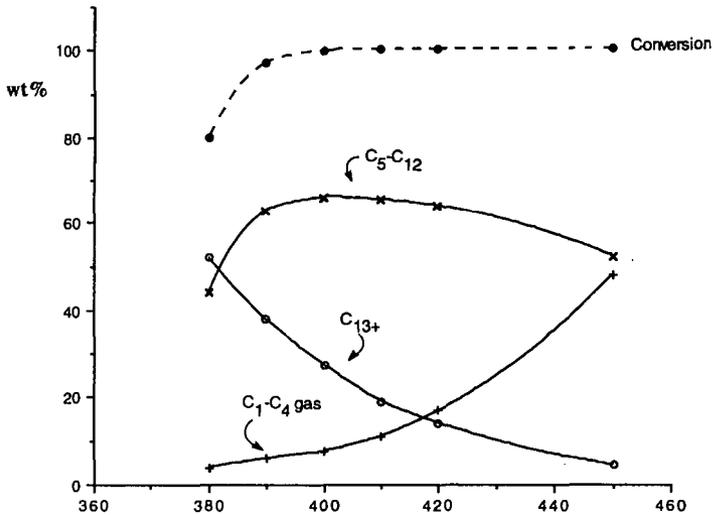


Fig. 1. Change in Product Composition from Depolymerization of Polypropylene as a Function of Reaction Temperature, °C.

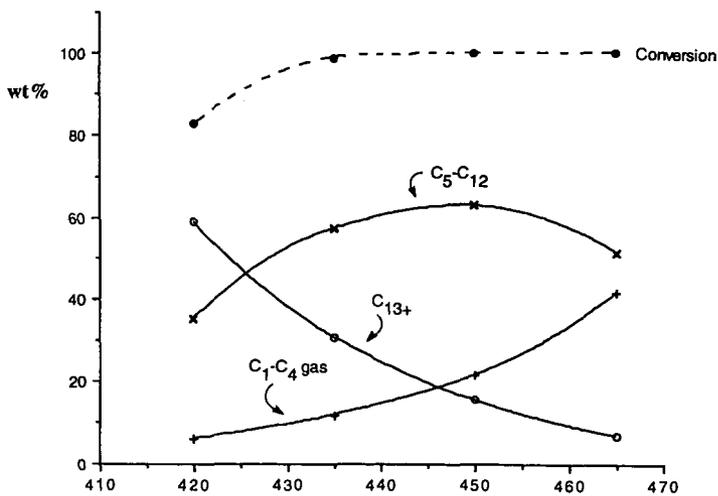


Fig. 2. Change in Product Composition from Depolymerization of Polyethylene as a Function of Reaction Temperature, °C.

