COLIQUEFACTION OF WASTE PLASTICS WITH COAL

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ABSTRACT

Polyethylene (PE), poly(ethylene terephthalate) (PET), mixtures of PE and PET with different coals,and actual plastic wastes from such items as milk jug and soft drink bottles were liquefied in a tubing bomb reactor. Comparative experiments were performed at 400-450°C for times of 15-60 min. at a cold hydrogen pressure of 800 psi. The experiments used two types of catalysts: highly dispersed iron based catalysts and an HZSM-5 zeolite catalyst. Saturated oil, consisting of mainly straight chain alkanes and minor alkenes, and some light hydrocarbon gases were produced from liquefaction of both the plastic and the plastic-coal mixtures. Using PE, PET, and samples prepared from waste milk jugs and soda bottles alone with the HZSM-5 catalyst, 100% conversion with oil yields of 86 to 92% were obtained. Using coal/plastic mixtures with a highly dispersed iron catalyst, which gives excellent results for coal alone, somewhat lower conversions (53-91%) and oil yields (26-83%) were obtained. Further studies are in progress to explore the optimum conditions for direct liquefaction of plastic wastes and coal, and to examine the effect of a variety of potential superacid catalysts such as zeolite and highly dispersed sulfated metal oxides (e.g. Fe_2O_3/SO_4^{2-} and Fe_2O_3-ZrO_2/SO_4^{2-}).

INTRODUCTION

In recent years, disposal of plastic wastes has become an increasingly serious environmental concern. Due to an ever increasing volume of plastic products, sanitary landfills can no longer continue to be the major means for plastic wastes disposal. Plastics recycling appears to be a possible alternative solution and has potential for high growth. However, the recycling of plastics that takes place currently is not due to industry initiatives, but because of government edicts. In the United States, laws are in effect in states such as California, Oregon, and Wisconsin that require plastic bottles to be made of at least 25 wt% of recycled plastic. Similar laws in other states and federal laws are likely to follow. In Germany, the law requires that 80% of plastic wastes must be recycled by 1995. France has just recently passed a similar law.

In 1990, about 0.4 million tonnes of plastics in the form of soft drink bottles entered the municipal waste stream, of which 31.5% was recovered. However, out of seven million tonnes of total plastic wastes in the same year, only 3.7% was recycled (Figure 1)[1]. Conventional plastic recycling always faces the problem of contaminated and mixed plastic scrap, which cause difficulties in the recycling. The potential exists for impurities to diffuse into products packaged in recycled containers. Aside from toxic concerns, these impurities could also damage the processing equipment. Further, the equipment conversion or replacement costs in order to use reclaimed plastics are high and may not be economical for a small plastic molding industry. In addition to all these obstacles in the way of using recycled resin in industry, the average price of virgin high-density polyethylene in the U.S. is currently 30 cents per pound, while the price of recycled high density polyethylene is 32-33 cents per pound[2]! Conventional pyrolysis, as an alternative for plastic waste recycling, usually results in unsaturated and unstable oils of low yield and low value that can be used only for combustion.

Considering current conditions and expected future trends, of all the options that exist for plastics recycling, liquefaction of plastic and rubber wastes should be considered seriously for efficient and economical plastics recycling. Liquefaction of plastic wastes can not only provide a solution for plastics disposal, but can also generate an environmentally acceptable transportation fuel. The current rate of plastic waste materials that are disposed in the United States each year constitutes a potential hydrocarbon resource from which over 80 million barrels of oil per year could be produced. Moreover, coliquefaction of plastic wastes and coal could yield synergistic effects. Unfortunately, very few investigations have been conducted in this area and much work needs to be done to develop liquefaction strategies for recycling plastic wastes.

EXPERIMENTAL

In our preliminary experiments, a medium density polyethylene (PE), poly(ethylene terephthalate) (PET), mixtures of PE and PET with different coals, and actual plastic wastes from such items as milk jug and soft drink bottles were liquified in a one stage tubing bomb reactor in a fluidized sand bath using two different catalysts. This set of experiments is designed to investigate the effect of catalysts on the total yield and product distribution in the liquefaction process. The tubing reactor is first charged with feed materials and pressurized to 800 psi with hydrogen (cold). The reactor is then connected to an agitation apparatus and heated to desired temperature in a fluidized sand-bath while being agitated with a vertical motion at 400 cycles per min. during the reaction period. The liquefaction products from these experiments were determined by Soxhlet extraction with toluene, tetrahydrofuran (THF), and pentane. Comparative experiments were performed for coliquefaction of mixtures of a medium density polyethylene (PE) and Blind Canyon coal and iron ion-exchanged Beulah lignite. The experiments used two types of catalysts: highly dispersed iron based catalysts and an HZSM-5 zeolite catalyst.

The quality of the oil products was examined using chemical analysis and gas chromatography. Extensive characterization studies are being carried out on the source materials, liquefaction products, and catalysts. A variety of analytical techniques are being used in these studies, including x-ray absorption fine structure (XAFS) spectroscopy, Mossbauer spectroscopy, x-ray diffraction (XRD), and transmission electron microscopy (TEM) for catalyst characterization.

RESULTS AND DISCUSSION

Saturated oils, consisting mainly of straight chain alkanes and minor alkenes, and some light hydrocarbon gases were produced from the liquefaction of both the plastic and the plastic/coal mixtures. The total conversion and oil yield for these experiments are listed in Table I. Using PE, PET, and samples prepared from waste milk jugs and soda bottles alone with the HZSM-5 catalyst, 100% conversion with oil yields of 86 to 92% were obtained. Using coal/plastic mixtures with a highly dispersed iron catalyst that gave excellent results for coal alone, somewhat lower conversions (53-91%) and oil yields (26-83%) were obtained. It is found that a mixture of iron ion-exchanged Beulah lignite[3] and polyethylene (in a ratio of 25:75) exhibits higher conversion than mixtures of 50:50 and 75:25 of these two components, but lower than that for pure polyethylene. Catalytic liquefaction experiments were carried out both with and without the presence of the solvent. Polyethylene in the presence of HZSM-5 catalyst on the other hand, exhibited higher conversion than either the polyethylene alone or mixture of polyethylene and superfine iron oxyhydroxide, implying synergistic effects. The quality of the oil products was examined using gas chromatography in collaboration with the UK Center for Applied Energy Resources (CAER) and the results for oil and gases produced during liquefaction of polyethylene are shown in Figures 2 and 3, respectively.

Further detailed studies are in progress to explore and establish the optimum conditions for direct liquefaction of waste plastics and coal, including the effect of temperature, pressure, reaction time, and coal/waste plastic ratio. The effect of a variety of potential superacid catalysts such as zeolite and highly dispersed sulfated metal oxide (e.g. Fe_2O_3/SO_4^{2-} and Fe_2O_3-ZrO_2/SO_4^{2-}) is also being investigated.

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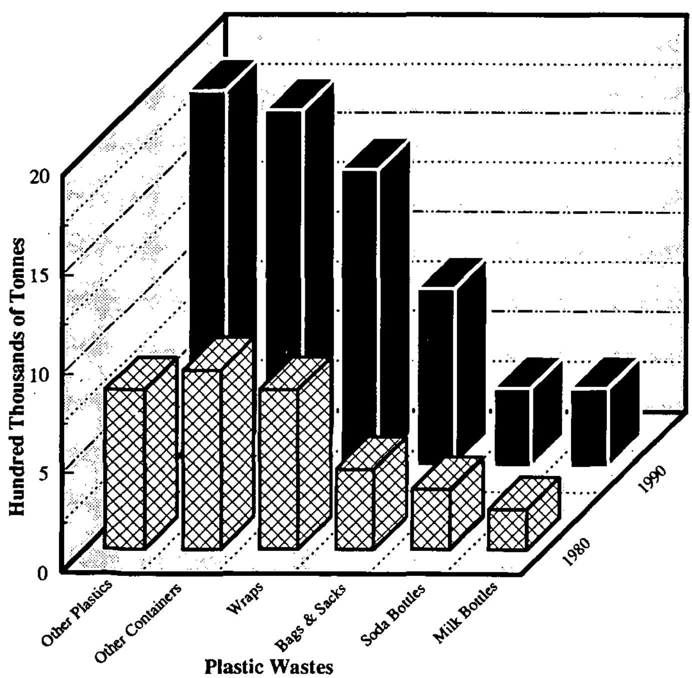

Figure 1. Characterization of Municipal Waste in the United States

Table I. Experimental results obtained from liquefaction of plastics, and coliquefaction of plastic/coal mixtures.

Sample	Additives	Temperature(C)	Total Conv.%	Oil Conv.%
PET	HZSM-5	420	100	92
PE	HZSM-5	420	100	88
PET	HZSM-5	400	100	90
Milk jug	HZSM-5	420	100	86
Coke Bottles	HZSM-5	420	100	93
lignite:PE 1:3	Fe-exch.+DMDS	450	91	83
lignite:PE 1:2	Fe-exch.+DMDS	450	67	51
lignite:PE 1:1	Fe-exch.+DMDS	450	53	40
PE	Tetralin	450	100	33
BC Coal:PE 1:1	Tetralin	450	70	42
BC Coal:PE 1:1	30Å FeOOH+DMDS	450	48	26
PE	30Å FeOOH+DMDS	420	100	76

PE = polyethylene, PET = Polyethylene Terephthalate, DMDS = Dimethyl Disulfide
BC = Blind Canyon coal, Fe-exch. = Iron ion-exchanged Beulah lignite

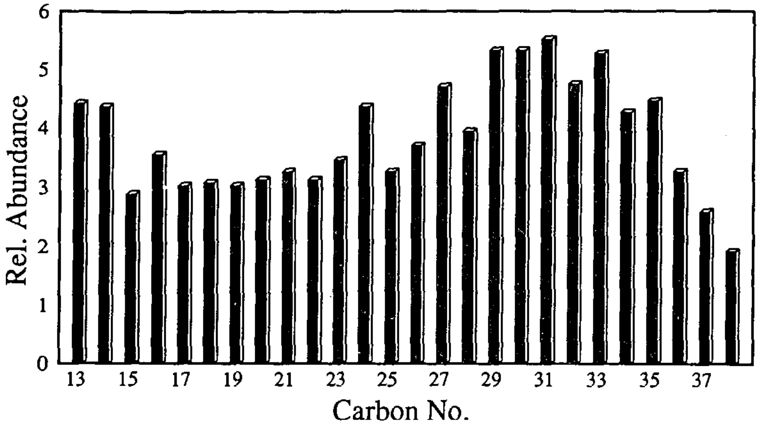

Figure 2. Pentane soluble products distribution of polyethylene

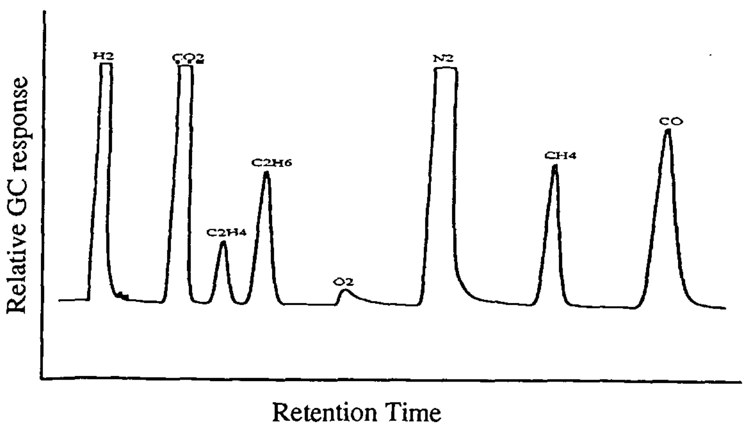

Figure 3. GC chromatogram of gaseous compounds produced during liquefaction of polyethylene