Available online at www.sciencedirect.com
SCIENCE DIRECT
J. Anal. Appl. Pyrolysis 74 (2005) 282–289
JOURNAL of ANALYTICAL and APPLIED PYROLYSIS
www.elsevier.com/locate/jaap

Thermal and catalytic decomposition behavior of PVC mixed plastic waste with petroleum residue

Mohammad Farhat Ali, Mohammad Nahid Siddiqui *

Department of Chemistry, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia

Received 24 June 2004; accepted 17 December 2004
Available online 9 March 2005

Abstract

The pyrolysis and hydropyrolysis of PVC mixed plastic waste alone and with petroleum residue was carried out at 150 and 350 °C under N_2 gas and at 430 °C under 6.5 MPa H_2 gas pressure. The behavior of plastic waste during thermal and catalytic decomposition has also been studied in single- and two-stage reaction processes. In the individual pyrolysis process, both the petroleum residue and polystyrene (PS) undergo more than 90% conversion to liquid and gaseous products, whereas low-density polyethylene (LDPE) and high-density polyethylene (HDPE) yielded lower conversions products, and polypropylene (PP) and polyvinyl chloride (PVC) afforded somewhere a moderate to high conversion products.

In a single-stage pyrolysis reaction, PVC was processed with petroleum residue at 150 and 430 °C, under N_2 gas for 1 h at each temperature in a glass reactor. The model PVC and waste PVC showed slight variations in the products distribution obtained from the glass reactor. In two-stage process, model PVC, vacuum gas oil (VGO) and a number of different catalysts were used in a stainless steel autoclave micro tubular reactor at 350 °C under the stream of N_2 gas for 1 h and at 430 °C under 950 psi (6.5 MPa) H_2 pressure for the duration of 2 h. Significantly, different products distributions were obtained. Among the catalysts used, fluid catalytic cracking (FCC) and hydrocracking catalysts (HC-1) were most effective in producing liquid fuel (hexane soluble) materials. The study shows that the catalytic coprocessing of PVC with VGO is a feasible process by which PVC and VGO materials can be converted into transportation fuels.

Keywords: PVC; Thermal and catalytic degradation; Fuel oils; Coprocessing; Residue upgrading

1. Introduction

The disposal of waste plastics has become a major environmental problem all over the world. USA, Europe and Japan generate about 50 million tons of post consumer plastic waste material. Saudi Arabia is one of the major producers of plastic in the world with total production capacity of around six million metric tons per year. The amount of plastic wastes in Saudi Arabia is about 15 wt% in the composition of domestic municipality waste [1]. The number of landfill sites is decreasing. Also land filling could result in plastic additives such as phthalates and various dyes polluting ground water. Incineration is an alternative to landfill disposal of plastic wastes, but this practice could result in the formation of unacceptable emissions of gases such as nitrous oxide, sulfur oxides, dusts, dioxins and other toxins. The option of secondary recycling or mechanical recycling, which is the reprocessing of plastic waste into new plastic products with a lower quality level, is not showing any signs of growth in the recycling industry. Tertiary recycling, which returns plastics to their constituent monomers or to their higher value hydrocarbon feed stock and fuel oil, is gaining momentum as an alternative method. Tertiary recycling includes all those processing which attempt to convert the plastic wastes to basic chemicals by the use of chemical reactions such as hydrolysis, methanolysis and ammonoloysis for condensation polymers and to fuels with conventional refinery processes such as pyrolysis, gasification, hydrocracking, catalytic cracking, coking and visbreaking for addition polymers excluding PVC. Pyrolysis of waste plastic affords high rates of conversion into liquid fuels that can be used as feedstock in refinery. There has been a lot of research work on the pyrolysis of individual

---

* Corresponding author. Tel.: +966 3860 2529; fax: +966 3860 4277.
E-mail address: mnahid@kfupm.edu.sa (M.N. Siddiqui).

0165-2370/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jaap.2004.12.010

and mixed plastics with and without PVC into liquid fuels [2–4].

One of the main problems in the pyrolysis of PVC and mixed plastics containing PVC is the production of hydrogen chloride, chloro organic and inorganic compounds during the early stages of pyrolysis process. The presence of such chloro compounds in the liquid products of pyrolysis are highly undesirable; therefore efforts were made to remove these halogen contents prior to pyrolysis of the waste plastics into liquid fuel products [5–7]. The behavior and the chemical nature of mixed plastics containing PVC are very important parameters to be known before carrying out dechlorination process. The kinetic studies on the decomposition of various individual and mixed plastics revealed that different molecular structures of the plastics undergo different reaction mechanisms of decomposition, follow different reaction rates and shows a different and great temperature dependency of the decomposition rate [8,9]. These studies suggest that the dechlorination of PVC occurs at relatively low temperatures via free radical mechanism. This tendency prompts the use of a combination of separation and decomposition of plastic waste in stepwise pyrolysis with different temperatures in the preliminary step for the dechlorination of PVC. During the dechlorination step, the rechlorination of other components of the product mixture must also be checked and avoided.

In this work, we report the pyrolysis of PVC mixed plastic waste alone and coprocessed with petroleum residue. The behavior of plastic waste during thermal and catalytic decomposition has also been studied in single- and two-stage reaction processes. The product distributions and the effect of catalyst types on percent conversion of plastics into liquid fuels are discussed.

2. Experimental

2.1. Materials

2.1.1. Polymers

The model plastic compounds, polystyrene (PS), low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP), polyethylene terephthalate (PET) and polyvinyl chloride (PVC) used in this study were obtained from Saudi Basic Industries Corporation (SABIC), Riyadh, Saudi Arabia, and were used as received. Municipal waste plastic (MWP) for PVC was collected locally as used water pipes and prepared in the laboratory by chopping and mixing for the reactions.

2.1.2. Petroleum residue

It is an atmospheric bottom residue from Arab light crude oil supplied by Saudi Aramco's Ras Tanura refinery. Arab light crude was found to contain a substantial amount of low boiling material (about 8% of <350 °C distillate). The atmospheric bottoms sample was charged to a wiped-film molecular still (Pope Scientific, Menomonee Fall, WI, USA) and more volatile part of the feed was progressively vaporized to remove the material boiling below 350 °C. This atmospheric bottom petroleum residue (350 °C+) was used with plastics in single-stage coprocessing reactions whereas a distillate fraction of the same petroleum residue with boiling range of 325–500 °C, called vacuum gas oil (VGO), was used in the two-stage coprocessing reactions.

2.1.3. Catalysts

The following eight different catalysts were obtained from the manufacturers and used in this work: hydro cracking catalysts (HC-1, HC-2 and HC-3), ZSM-5 zeolite catalyst, FCC catalyst, presulfided NiMo/Al_2O_3 (NiMo) catalyst and iron oxide carbon composite catalyst. Selection of suitable catalysts for the cracking reactions was the difficult task due to limitations in terms of operating conditions, feedstock properties, catalyst performance and desired products. The suitability of catalysts was based on these essential characteristics: activity, selectivity, ease of regeneration and mechanical strength. The catalyst selection for this study is based mainly on the results obtained in our previous work [2].

2.2. Analytical procedure

The procedure can be explained in two parts: first to determine the HCl contents in PVC and secondly the fuel oil formation in the form of hexane, toluene and THF solubles in the reaction material.

A stock solution of 1 M NaOH was prepared and standardized using potassium hydrogen phthalate solution in order to obtain the exact concentration of NaOH solution that was found to be 0.96 M.

Fig. 1 shows the schematic of a fixed-bed pyrolytic gas-purged glass reactor used to pyrolyze the PVC plastics. The reactor is a Pyrex glass tube with 32 cm length and 2 cm i.d. The samples were placed inside the tube before reaction started. A programmable temperature controller controlled the furnace. This enabled the samples to be heated slowly at the rate of 5 °C/min until temperature reaches to 150 °C. This temperature was maintained for 1 h to ensure that all HCl gas was evolved. Then heating was increased at the same rate to the final pyrolysis temperature of 430 °C. The sample was held at 430 °C for another hour or until there was no significant evolution of gases. The liquid oil phase was trapped in a cylindrical flask using a cold-water spiral condenser. Nitrogen gas was used as the carrier gas at a fixed flow rate to sweep the evolved gaseous products quickly. The gases evolved, except HCl, were not collected so no gas analysis was performed. Initially, 200 ml of standard NaOH solution was used to trap and determine the amount of HCl gas produced from the pyrolysis. At the end of the reaction, the glass reactor was cooled and weight of the reactor and the cylindrical flask