

CHAPTER I

INTRODUCTION

In the future, increasing shortages of crude oil and natural gas will cause a world-wide search for new energy sources, power fuels and chemical raw materials. Recently, waste plastic products, especially polyolefin wastes, have become increasingly important as raw materials to provide hydrocarbon fuel oil due to continuously increasing growing quantities of waste. [1] Therefore, it is another way to reduce plastic waste that has become a serious environmental problem.

The growth rate of using polypropylene (PP) is increasing because PP is widely used in packaging, transportation and furniture. It was forecasted that consumption of PP in the world during 1997 would be 17,850,000 metric tonnes, in the third place among the commodity plastics, after polyethylene (PE) and polyvinylchloride (PVC) but before polystyrene (PS). [2] In Thailand [3], PP consumption during 1993 was 300,000 metric tonnes. This had grown at an annual rate of 21 percent between 1989 to 1993. It could be estimated that consumption during 1997 would be 500,000 metric tonnes at a growth rate forecast of approximately 14 percent.

The consequence of increasing consumption of PP are the enlargement of the amount of used PP such as from battery cases due to the multiplying numbers of cars, tractors, ships etc. Due to the toxicity of lead, landfill disposal of battery cases is banned. The problem can be solved by the establishment of a battery recycling industry to reuse the lead. The by-product from battery recycling is the battery case made of impact PP. In the United States during 1990, the post consumer amount of polyolefin resin

derived from battery cases was estimated to be 45,000 tonnes. Some used PP was reclaimed from these cases, approximately 40% (18,000 tonnes), was used to manufacture new battery cases or for automotive production whereas the use of the remainder of this material is not well documented.[4]

Generally, most of PP waste is disposed in landfill or by incineration, but these methods have become increasingly difficult because of the diminishing availability of disposal space, strengthened governmental regulations and growing public concern about hazard to the environment. Direct incineration would lead to increase greenhouse gas emissions, primarily carbon dioxide, and particulate pollutant, while direct mechanical recycling of plastic gives a downgraded appearance in comparison with virgin plastic. Moreover, mechanical recycling produces objects that will eventually require discarding due to brittleness caused by oxidation and exposure to UV light.[5] Several alternative approaches requiring more processing than these method have been proposed in order to deal more effectively with the increasing volume of plastic waste. Tertiary recycling, the further development of recycling, involves chemical transformations or degradation of the plastic to a new product, gaseous hydrocarbon, syn gas and hydrocarbon oil. [6]

The efforts for further promoting the tertiary recycling of used PP into hydrocarbon oil are being exerted by studying new processes or new catalysts to produce high yields of hydrocarbon product. For instance, Stapp [7] studied a process for converting municipal waste containing plastics to a synthetic crude oil which consisted of gasoline, diesel fuel and gas oils by catalytic cracking. He showed that the presence of cellulose and proteinaceous waste materials in the MSW does not inhibit the process.

The municipal waste was heated with molybdenum in a mixture of hydrogen sulfide and hydrogen at 350°C-450°C and 750-3,000 psig for 15 minutes to 8 hours, depending on the percentage of plastics. The

minutes to 8 hours, depending on the percentage of plastics. The disadvantages is from the use of H_2S when oxygenates or nitrogen-containing compounds was in the feed as a result it requires hydrotreating before isomerization to produce the diesel containing sulfur. In addition, because of the limitation of HDPE content for operating at temperature below $400^\circ C$, the efficiency in recycling the plastic wastes was restricted.

Butcher, Jr. [8] studied a method for cracking polymeric materials such as PP, PE, PVC, PS otherwise amenable to cracking by alkali fusion. This method used of a molten reaction mixture of NaOH and KOH pellets, Cu_2O and the polymeric substances, in the ratio of 10:10:1, at reflux temperature ($250^\circ C$) for sufficient time to depolymerize the polymeric substances, in a 400 ml. copper vessel equipped with pyrex apparatus. The addition of NaOH into molten plastics caused an immediate frothing and foaming and cracking initiated.

This method produced only 40-50% yield of mixture of kerosene and diesel fuel whereas it produced over 16% yield of wax.

Conversion of plastic waste into hydrocarbon oil using two reaction stages, thermal cracking and catalytic cracking was studied by Takahashi and Tanimoto. [9] Waste plastics (PP, PE, PVC and rubber wastes) were heated so as to be thermally decomposed at $250-450^\circ C$ and to produce a vapor product containing oil and gas components. The vapor product was brought into contact with 30-80% weight of aluminium trichloride ($AlCl_3$) and hydrochloric acid as a decomposing activator at $180-250^\circ C$ to produce decomposed oil 45-40%wt.

This method was not appropriate due to the reduction of temperature when the vapor product passed through the catalytic cracking stage. Waxes from the condensed vapor product would plug the catalyst and cause the reduction of its activity.

To dissolve the plug of waxes and to increase the oil yield from their method without using hydrochloric acid, Takahashi, Tanimoto, Muraoka and Fukushima [10] developed a method of obtaining hydrocarbon oil from waste plastic by employing zeolite and sulfuric acid. The thermal cracking product at 450-550°C was liquefied and then the liquid phase cracking reaction of the liquefied product was caused by using zeolite to produce hydrocarbon oil at 200-350°C.

Although the problem was solved with increase of oil yield, this process consisted of two reaction stages which operated under vigorous conditions and still employed acid, H₂SO₄. The development from a two stage reaction to a one stage reaction stage was done by improving the efficiency of the catalyst, aluminium oxide, aluminosilicate, zeolite or dual function catalyst. For instance, Zmuda [11] produced liquid fuels from used products made of PP, PE and PS by cracking of polyolefins over catalysts. The catalysts were introduced into the system in the form of aluminium oxide, aluminium silicate or aluminosilicates of alkali metals or alkali earth metals in amount of 1-5% by weight and the mixture was heated to a temperature between 400-600°C. Profitably, during the reaction air could be introduced into a system in amounts of 0.02 to 0.04 m³ per 1 kg.. This method produced 98.0% of petro types or diesel type fuels.

Intrapreecha [12] reported the hydroisomerization reactions of High Density Polyethylene wax in the presence of catalyst (5-9 weight%), at temperatures of 300-400°C under hydrogen pressure of 300-500 psig. for 10-240 minutes. A Platinum-fluoride-alumina catalyst containing 0.3 % Pt and 0.5% F was used to produce low speed diesel in a yield of more than 90 %weight.

Leesuksan [13] prepared four types of dual functional catalyst Platinum-Fluoride, Platinum-Tin-Fluoride, Nickel-Tin-Fluoride and Cobalt-Tin-Fluoride on alumina support for catalytic cracking of used polyethylene to produce C₁₀-C₁₆ liquid hydrocarbons with gasoline properties. She found that Platinum(0.6%)-Tin(0.15%)-Fluoride(0.15%) gave the best results with a yield of 94% at 400°C, under 600 psig. hydrogen for 12 hours.

The results from Zmuda and Leesuksan showed good hydrocarbon oil yields can be obtained using alumina, alumino silicate type catalysts in a one step reaction.

Objectives and Scope of the Research

The goal of this research is to investigate catalysts that are more effective and cheaper than Pt, to lower condition by using other catalysts, iron, cobalt and nickel, combined with tin and fluoride in catalytic hydrocracking reactions of used PP into hydrocarbon oil in one reaction stage. Furthermore, this research aimed at investigating the support of the catalyst by choosing Al₂O₃ and molecular sieve which are cheaper and more available than zeolite and comparing the results. The effect of catalyst concentration, temperature, reaction time was examined, and the variation in H₂ pressure in the batch reactor was considered. Because of its importance as a feedstock for petrochemicals and oil, yields in short times were emphasized in this work. The physical properties of the oil product from the optimum conditions were tested according to the ASTM standards.