



Hydrocracking of virgin and waste plastics: A detailed review

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ABSTRACT

The continuous increase in the demand for plastics is causing severe problems of managing increased waste plastic generation. The hydrocracking of plastic materials is considered an important method of converting these wastes into liquid fuels of high quality. Many attempts have been made in the search for a suitable catalyst and optimum operating conditions required for a successful hydrocracking process. In the present work, a review of the literature regarding hydrocracking of both virgin and waste plastic materials is carried out. The effects of various hydrocracking variables such as temperature, hydrogen pressure, reaction time, catalyst presence and type, and type of feed plastic employed are discussed in detail. A few hydrocracking mechanisms relevant to plastic degradation reported in the literature are described and an exhaustive database of the experimental work is compiled.

1. Introduction

The production of plastic materials such as polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), and polyvinyl chloride (PVC) is increasing each year [1] due to their consumption in packaging, construction, agriculture, electrical and electronic appliances, and health care applications [2]. Plastics have some unique characteristics, such as outstanding versatility, light weight, firmness, resistance to water, and low cost, which make them indispensable for modern civilization [3,4]. However, the life span of most of the plastic items is very short and most of these items have a life time of less than one month [5,6]. Due to poor biodegradability rates [6–10], the plastic waste occupies the land for a longer period of time [10,11] as only 1–3 wt% of the hydrocarbon contents of plastics are degraded in 100 years [10]. The plastic waste, therefore, reduces the overall landfill volume and becomes a huge environmental problem. Landfill sites are decreasing [10,12–16] and the cost of landfilling is soaring [15–17]. New legislations in some countries require a decrease in the amount of waste plastics sent to landfill sites [6,10]. In a landfill dump, plastic material is an environmental burden, a waste of resource, source of pollutants such as stabilizers, and greenhouse gases such as methane [10,18,19]. Incineration of this plastic waste to produce energy results in the emission of particulate matter [18,20,21] and harmful gases including unburned hydrocarbons, nitrous and sulfurous oxides, and dioxins and furans [19,22–24] that are highly unacceptable from the environmental point of view. Incineration and landfilling are

therefore not the preferred routes for plastic waste management and plastic waste needs to be treated in a more sustainable and environmentally friendly way.

Recycling is an alternate method to disposal in a landfill or incineration. It not only protects the environment [25,26], but also helps to convert the potential resource to useful products [26–28]. Among the various recycling methods, tertiary recycling, in which waste plastic material is converted to petrochemicals and fuels [15,29,30] is gaining increased attention worldwide [8,15,18,22,29,31,32]. Tertiary recycling is an economical and environmentally friendly way of recycling plastic and is recognized as the most promising method among the various waste plastic management methods [1,4,33,34]. Tertiary recycling is carried out either by a chemical or a thermal recycling technique [29,35]. Condensation polymers such as polyesters and polyurethanes are subjected to solvolysis such as glycolysis, methanolysis, and hydrolysis [15,18,29,32,36], whereas addition polymers (PE, PP, PS, and PVC) are subjected to thermal methods such as gasification, thermal cracking or pyrolysis, catalytic cracking, and hydrocracking [15,18,32,37,38].

Gasification is a process which is carried out in the presence of reduced amount of oxygen, air, or steam, to produce mainly a synthesis gas, i.e., a mixture of CO and H₂. Cracking is a process in which heavy polymeric molecules are broken down into smaller much lighter molecules of gaseous and liquid range. Cracking can be carried out in the presence or absence of hydrogen and with and without the use of a catalyst. Thermal cracking or pyrolysis is usually carried out at elevated

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temperatures and in the presence of an inert atmosphere such as nitrogen. Catalytic cracking essentially requires a catalyst, usually an acidic catalyst, to carry out the process at a lower temperature and to improve the yield as well as quality of the product. The process of cracking in the presence of hydrogen is called as hydrocracking.

The hydrocracking process is employed for the conversion of heavy (high boiling) plastic molecules to lighter (low boiling) molecules and occurs in the presence of hydrogen through carbon-carbon bond cleavage, together with simultaneous or successive hydrogenation of unsaturated molecules formed during the process [39–41]. Hydrocracking is one of the most promising methods used for the conversion of waste plastics into high quality liquid fuels. It is more advantageous compared to pyrolysis and catalytic cracking as it delivers a highly saturated liquid product [42,43] that is directly used, without subsequent processing, as a transportation fuel or a fuel oil required for energy production. Pyrolysis and catalytic cracking are considered to give unsaturated hydrocarbons [42], a large amount of coke [42], and a product with wide molecular weight distribution [44]. The application of hydrocracking reactions involves lower process temperatures [45] and reduced amounts of olefins [33,43,45–47], aromatics [43,47], and coke formation in the reaction products. Furthermore, the presence of hydrogen results in the removal of heteroatoms such as chlorine, bromine, and fluorine that may exist in waste plastic [2,5,48].

Hydrocracking of a polymer generally occurs in the presence of a bifunctional catalyst in a stirred batch autoclave [49], at moderate temperatures and relatively high hydrogen pressures. Typical hydrocracking conditions are 300–450 °C and 2–15 MPa cold hydrogen pressure. Heat energy is required to bring about the reaction contents to the desired temperature and to crack the long hydrocarbon chains. From an energy perspective, cracking and hydrogenation are complementary reactions, as cracking is an endothermic reaction, while hydrogenation is an exothermic reaction [10]. High partial pressure of hydrogen should be used in order to suppress undesirable coking or repolymerization [50]. Although non-catalytic hydrocracking (thermal hydrocracking) can possibly be realized, however, the presence of a catalyst is needed to stimulate the hydrogen addition. Any catalyst used for the hydrocracking of waste plastic must have a cracking function and a hydrogenation-dehydrogenation function. A typical hydrocracking catalyst has an acidic support with metal impregnated over it. The acidic support is responsible for cracking and isomerization reactions, whereas the hydrogenation-dehydrogenation function is performed by the metal loaded over the catalyst. The acidic support is usually an amorphous oxide such as silica-alumina, crystalline zeolite such as HZSM-5, a strong solid acid such as sulfated zirconia, or a combination of these materials [39]. The metal can be a noble metal (palladium or platinum) or non-noble metal of group VI-A (molybdenum or tungsten) and group VIII-A (cobalt or nickel) of the periodic table [39].

A hydrocracking process can be used in the direct liquefaction of plastic materials or in a two-stage liquefaction process where plastic material is first pyrolyzed, i.e., thermally cracked [15,38,51–61], catalytically cracked [51], or hydrocracked [45] and then the resulting product is subjected to hydro-treatment to improve the quality of the final liquid produced. Although not cost effective, in a two-stage process, deactivation of the catalyst by coke deposition and heteroatoms (e.g., N, S, Cl) is decreased [58] and reduced amounts of olefins are produced [58], allowing the fuel product, after the second stage, to be directly used in an automobile engine. Moreover, dechlorination of PVC materials can be carried out in the first stage to avoid the presence of chlorinated compounds in the final liquid fuel produced. Some researchers have also adopted co-processing schemes and carried out hydrocracking of a mixture of plastic and a co-feed such as coal [25,44,62–75]; biomass [76]; and oil residue, wax, waste lube oil, long chain alkane (e.g., n-hexadecane), or tetralin [15,21,25,44,65,68–73,77–85]. Co-processing is useful in increasing the plant capacity to make it more economical.

In the present contribution, the literature study related to the hydrocracking of a plastic material by a direct liquefaction process and in

the absence of a co-feed material is reviewed in detail. The effect of various operating variables is surveyed and a comprehensive database of the experimental findings is developed. The objective is to critically review the operating conditions and the catalytic materials used for the hydrocracking reaction and to give appropriate recommendations for their use.

2. Survey of direct liquefaction of plastic materials by hydrocracking

Hydrocracking of virgin and waste plastics using a direct liquefaction process without the addition of a co-feed has been studied by a wide range of investigators. A number of these researchers studied the hydrocracking of a single type of plastic material, while others studied a mixture of individual plastics. The hydrocracking reactions were studied both in the presence and absence of a catalyst and the effects of various operating parameters, such as temperature, hydrogen pressure, reaction time, catalyst type, and catalyst loading were also studied. The hydrocracking reactions were generally carried out in a closed tubing bomb (shaking type) reactor or batch stirred autoclave, where the feed and catalyst were initially charged and hydrogen pressure was set in cold conditions. The products of the reaction were analyzed for gas yield, oil yield (lower molecular weight liquid fraction obtained by extraction using a solvent such as n-pentane, n-hexane, or n-heptane), total liquid yield that included pre-asphaltenes and asphaltenes obtained usually by tetrahydrofuran (THF) extraction, and solid residue. In a few studies, unreacted polymer and coke content were also measured. GC-MS and GC-FID were used to identify and quantify the product components and simulated distillation was carried out to develop a relationship between the boiling point temperature and the percent distilled. The relationship was later used to evaluate the yields of low boiling and high boiling fractions of the oil obtained. Table 1 shows the list of investigators along with the reaction conditions, catalysts, and analysis techniques employed, whereas Table A-1 in Appendix A is an extensive database of their experimental findings. The tables include only those studies that involve the direct liquefaction of a plastic material by hydrocracking reaction, without the addition of any solvent, waste oil, heavy oil, coal, or biomass. In the sections to follow, the ratios and percent values, such as catalyst loadings and yields, are reported by weight and hydrogen pressures are at cold conditions unless clearly stated.

2.1. Effect of reaction parameters on hydrocracking of plastic materials

2.1.1. Effect of catalyst on plastic hydrocracking

Catalysts play a key role in plastic hydrocracking. As discussed earlier, a bifunctional catalyst is usually required for this purpose. The presence of acidic function as well as hydrogenation-dehydrogenation function is normally required for achieving appreciable conversion, high yield and superior quality of liquid products, and reduced amount of coke deposits. A metal supported solid acid such as sulfated zirconia or zeolite is a good choice for this type of reaction. A suitable catalyst yields a liquid product that has a lower boiling point with greater iso- to n-alkane ratio and a lower bromine number (reduced quantity of olefins). Different types of commercially available and development catalysts designed for cracking, hydrocracking, and hydrotreating processes are used in the literature, to observe their effectiveness in hydrocracking of a plastic material.

Venkatesh et al. [42] employed ZrO_2/SO_4 , 0.5%Pt/ ZrO_2/SO_4 , 2.0% Ni/ ZrO_2/SO_4 , and 1.0%Pt/ $\gamma-Al_2O_3$ catalysts for the hydrocracking of HDPE (high density polyethylene), PP, and PS. No experiment was performed in non-catalytic conditions for the comparison. For the hydrocracking reaction of HDPE at 375 °C and 8.38 MPa H_2 pressure (reaction time of 25 min and feed to catalyst ratio of 5:1) over 0.5%Pt/ ZrO_2/SO_4 and 2.0%Ni/ ZrO_2/SO_4 , virtually the same conversion was obtained on each catalyst. In both cases, high iso- to n-alkane ratios

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