Pyrolysis of Polystyrene Waste

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The manufacturing of polystyrene around the globe has escalated in the past years due to its huge applications in various areas. The perpetual market needs of polystyrene led the polystyrene wastes accretion in the landfill causing environmental deterioration. The soaring need for polystyrene also led to the exhaustion of petroleum, a non-renewable energy source, as polystyrene is a petroleum-derived product.

polystyrene pyrolysis fuel oils

1. Introduction

For the past fifty years, plastic has played a crucial role in upgrading the human society [1]. It has imparted impulse in the development of numerous sectors like packaging, electronics, automobiles, medical, construction, etc. [1]. Due to the swift surge in the global population, the market need for plastics has risen. Owing to this, the total manufacturing of plastic throughout the world attained approximately 359 million tonnes in 2018 [2]. The regular increase in the requirement of plastic led to plastic waste accretion every year. Based on 2013 data, plastic scrap amounting to approximately 33 million tonnes was produced in the US [3]. As far as Europe is concerned, around 25 million tonnes of plastic finally turned out as scrap in the year 2012; out of this waste plastic approximately 38% accreted in the landfill, 26% was recycled whilst 36% was recovered through energy recovery technique [4]. These data signify that the quantity of plastic scrap that has accumulated in the landfill is too large. As a fact, natural degradation of plastics may take billions of years since its molecules constituting carbon, hydrogen, nitrogen, and chlorine are attached through very strong bonds [5]. Consequently, the regular accretion of plastic in the landfill poses a severe environmental hazard. To curtail the accumulation of plastic in the landfill, researchers developed techniques to recycle it [6]. However, recycling the plastic turns out to be a cumbersome and costly process since it requires excessive labor to sort out plastics and also results in water contamination [7]. Sorting of plastics is required before recycling as different plastic polymers have their characteristics such as resin compound they are constituted of, color, and transparency. The energy recovery technique is another method that transforms plastics directly into useful forms of energy and chemicals for industries since plastics are mainly derived from petroleum.

One of the most important and widely used plastic is polystyrene (PS) which is cheap and hard. It is transparent but can be colored by introducing colorants. It is heat resistant, lighter in weight and, exhibits good strength and durability that make this polymer fit for a variety of applications. The range of applications includes packaging, toys, and household items like computer housing and kitchen appliances, etc. PS are available in expanded and solid forms, and both of these forms are recyclable. However, expanded polystyrene foam waste loses its foam characteristics once recycled. It is possible to re-gas the recovered polystyrene, but it makes the product costlier than the virgin material. Thus, it is utilized in solid state in molding processes.

Expanded and solid PS scraps have been easily recycled to extruded plastic lumber. This extruded polystyrene (XPS) has been widely employed to construct windows systems, roof trusses and flooring of buildings and houses. Recycled PS is employed to manufacture plant pots, pens, and pencils, etc., whereas PS foam is used extensively as an insulator. Expanded PS can also be utilized as substrates to produce poly-electrolytes which display better flocculation characteristics compared to that of commercial Praestol 2515 [8].

Recycled and virgin PS are being employed to produce a material with practically the same properties as that of wood. This novel material exhibits striking resemblance to wood in respect of physical appearance, density, and structural properties, making it a suitable candidate that can replace wood in furniture and construction industry. Non-foam polystyrene materials also known as high impact polystyrene (HIPS), oriented polystyrene (OPS), Styrofoam, post-industrial products and post-consumer products are accepted as recyclable materials [9].

A large portion of the PS waste is disposed as solid pollutant in the developing countries. Moreover, the increased use of PS in electronic gadgets has rapidly enhanced the waste from electrical and electronic equipment (WEEE) which makes the situation more problematic. In addition, a large amount of expanded PS is routinely disposed at wholesale markets, supermarkets, departmental stores, restaurants, and shops, as well as machine manufacturing factories. It is later gathered by the recycling agents as a recycling resource. However, a number of issues have to be taken into consideration by the industries before recycling PS, such as, eco-friendliness, corporate social responsibility, hygienic prospective, and traceability. Prior to recycling, the waste materials must be washed properly to remove any stuck food or dust particles, the metallic caps and glass jars must be separated from the raw materials, and oversized commodities must be crushed so as to fit them into the bin and transporting truck easily. The volume of the PS waste can then be reduced by various techniques like dissolving into solvent, heating, and pulverizing.

The conventional method for the treatment of polystyrene is pyrolysis, which involves thermal decomposition without air to produce pyrolysis oils or gases and monomer or other valuable chemicals [10]. The pyrolysis process requires proper reactor and catalyst selection that control the pyrolysis temperature and end-products. A lot of researchers have devoted their study on the investigation of influence of reactor design (such as, batch-type, fixed-bed, continuous flow and pressure reactors) and material [11][12][13][14][15]. The utilization of solvents, various plastic blends and additives for carrying out pyrolysis is also found to be a promising method to optimize the yield of liquid products [16][17]. A lot of work has been focused on the pyrolysis of PS employing acidic and basic catalysts to enhance the yield and selectivity of products, and achieve a cheap pyrolysis method [18][19][20][21][22]. This review article deals with all the above issues, and presents an exhaustive up-to-date survey of the various methods employed so far to carry out pyrolysis of PS waste. Thus, it will be extremely useful for the scientists who are researching in this broad area to identify the fundamental issues and the major contributors. The prime and fundamental purpose of presenting this review article is to provide researchers and readers with a legible and unambiguous synthesis of the best resources available in the literature pertinent to the pyrolysis of PS waste.

2. Pyrolysis of Polystyrene

Polystyrene (PS) is made up of styrene monomers obtained from the liquid petrochemical. It comprises of a long hydrocarbon chain with phenyl groups linked to alternating carbon atoms. Presently, most of the polystyrene waste is disposed to the landfills and not recycled because of the problems encountered while separating and cleaning polystyrene. This creates a threat to the environment and causes damage to human beings, wild and aquatic life. Thus, it becomes very important to convert polystyrene into valuable products through pyrolysis. The pyrolysis process involves heating plastic at a high temperature of 300–900 °C in the absence of oxygen, wherein the long polymeric chains get decomposed into useful low molecular weight liquid and gaseous products. Oil, gas, and char are the three basic byproducts that are finally produced during pyrolysis. These byproducts are very useful in the production and refining industries. The produced liquid oil offers wide applications as fuel in furnaces, turbines, boilers, and diesel engines without any further treatment.

Pyrolysis is considered to be very flexible since involved parameters can be altered easily to obtain an optimum yield of the product. In contrast to the recycling process, pyrolysis does not cause water pollution and hence is considered eco-friendly technology [23]. Pyrolysis process had received a lot of attention from the scientific community since this process can finally produce liquid oil up to 80 wt.% at an easily achievable temperature of about 500 °C [24]. The pyrolysis of PS in a batch pressurized autoclave reactor had been reported by Onwudili et al. [25]. They carried out pyrolysis for one hour at a temperature range of 300–500 °C with a rate of heating at 10 °C/min and variation of ambient pressure from 0.31 MPa to 1.6 MPa. They noted that the pyrolysis of PS resulted in the production of approximately 97.0 wt.% liquid oil and maximum gas production of 2.5 wt.% at an optimum temperature of 425 °C. Such a high production of liquid oil was also reported by Liu et al. during the pyrolysis of PS employing a fluidized bed reactor at a temperature range of 450–700 °C. The observed record production of liquid oil was 98.7 wt.% at 600 °C. However, Demirbas at al.[26] reported that liquid oil production decreased to 89.5 wt.% when the pyrolysis was carried out in a batch reactor at 581 °C. Thus, it is not recommended to carry out pyrolysis of PS at a temperature exceeding 500 °C to achieve maximum liquid oil production.

To sum up, the production of liquid and gaseous by-products from the pyrolysis of polystyrene relies mainly on the reaction conditions. Catalytic pyrolysis using suitable catalysts can sway the yielded products and their distribution, in addition to the reduced reaction temperature. This advantage leads to the high contents of products having higher commercial value [27][28]. Polystyrene could be converted into styrene over catalysts by simple thermal cracking at relatively low temperatures. The pyrolysis of polystyrene mainly depends on the reaction conditions such as temperature, reaction time, reactor type, the presence of catalysts, etc. At low temperatures, products mainly consist of liquid compounds (mono aromatic). At higher temperatures, gas and coke yields are higher and the liquid fraction has significant aromatics (dimer, trimer) [27][28][29][30]. The pyrolysis of polystyrene had been previously investigated at a comparatively lower temperature ranging from 370 °C to 400 °C employing a batch-type stirred reactor. The main products were single aromatic species (styrene ca. 70 wt.%, α-methyl styrene, toluene) and double aromatic species (1,3-diphenylpropane and 1,3-diphenylbutene) [29]. The pyrolysis of polystyrene in a fluidized-bed reactor at 550 °C generated the residue that contains 19–20% for oil yields and 10–11% for styrene monomers [31][32]. Thermal decomposition of expanded polystyrene in a pebble bed reactor at 500

°C produced 91.7% of liquid products while yielding 85.5% of styrene using ceramic pebbles. Several studies have been conducted on catalytic pyrolysis of polystyrene over different solids like metallic oxides (silica-alumina,, alumina or silica supported transition metals) [33][34], zeolites (, dealuminated HY) [32][33][34][35], mesoporous materials (from natural sepiolite) [36][37], and clays (halloysite, albite, montmorillonite, and pyrophyllite) [38][39]. The use of catalysts in the pyrolysis of polystyrene waste determines the good selectivity for the formation of costly hydrocarbons and the use of lower temperatures. Thus, the search for “cheap catalysts” for pyrolysis is of particular interest from an industrial and economical point of view [40]. The catalyst cost, type, and its amount represent key factors in determining the economy of catalytic processes because, in a continuously operating plant, it is necessary to have a large amount of catalyst. Mostly, natural catalysts are employed since their textural properties, such as surface area, particle size, and pore size distribution play an important role in end-product distribution. In this review, we will focus on the influence of temperature and type of catalysts on the yields and distribution of end products in thermal and catalytic pyrolysis. Furthermore, we have also surveyed a recent method to conduct the pyrolysis process in the presence of a solvent in pursuit to optimize the quality and quantity of oil produced [41]. Table 1 summarizes the main advantages of the various methods employed for the pyrolysis of PS.

Table 1. Advantage of various methods employed for PS pyrolysis.

S. No.	Methods for Polystyrene Pyrolysis	Advantages	Ref.
1.	Classical Heating Method		
	i. Batch Reactor	high conversion efficiency	[42]
	ii. Fixed Bed Reactor	simplicity in design	[43]
	iii. Fluidized Bed Reactor	a) yield of liquid products is more than 90wt.%. b) formation of gas and coke is relatively insignificant.	[12]
	iv. Conical Spouted Bed Reactor	a) allows better blending of charge b) can treat large particles with density disparity	[44]

	v. Free-fall Reactor Under Vacuum	produces important liquid chemicals such as benzene, toluene, and naphthalene besides styrene monomer and valuable gaseous output.	[45]
2.	Microwave-Assisted Pyrolysis	a) extremely rapid heating b) higher production rate c) low production cost d) energy saving	[46]
3.	Catalytic Pyrolysis	a) decreases the operating temperature needed for the pyrolysis b) reduces the heat energy requirement c) favors the industrial application of pyrolysis d) produce final products of commercial significance	[47][48]
4.	Solvent-Assisted Pyrolysis	a) high heat and mass transfer rates b) reduces operating temperature c) higher liquid yields	[49][50]

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