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Plastic Waste Management System Using Super-Critical Water

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Abstract

This review paper aims to understand the green impact and highly promising potential that a Supercritical Water (SCW) system holds for the degradation of wastes, plastic polymers to be more particular. It is known how menacing it can be to treat and safely dispose of waste plastics. Hence this paper tries to analyse an alternate green way to do the same. This study explores the degradation of plastics using SCW, investigating its potential as an eco-friendly method. An effort is made first to understand the working principle of SCW setup and then a comparative analysis and study is made for plastics being treated under SCW conditions and their plausible outcomes. Polymers that have been studied are Polyethylene Terephthalate (PET), ABS polymers, Polycarbonate (PC), High-Intensity Polystyrene (HIPS), Polypropylene (PP) and Polystyrene (PS). Upon degradation, each feedstock plastic got broken down into its parent monomers and some of them underwent gasification to give gaseous products. The monomers further degraded after prolonged heating and gave a mixture of by-products. Results indicate promising avenues for utilizing SCW as a means to address plastic pollution and contribute to environmental sustainability.

Keywords: Supercritical Water (SCW), Plastic waste management, Polyethylene Terephthalate, ABS Polymer, Polycarbonate, HIPS Polymer, Polypropylene, Polystyrene

1. Introduction

We have had a problem with waste ever since the Industrial Revolution. The rise of automation, fuelled by technological advancements, has significantly impacted the environment. Waste production is an inevitable consequence of our daily activities. This includes trash or garbage from industries, hospitals, households, schools, offices, marketplaces, restaurants, and other public places. Our daily lives create a mountain of waste, from leftover food scraps and used plastic bags to discarded soda cans, water bottles, broken furniture, appliances, and clothing.

Wastes according to the degradation processes are classified into two categories: i) biodegradable wastes (capable of being decomposed by bacteria or other living organisms. Different vegetable waste, food waste, paper waste, biodegradable plastics, human waste, manure, sewage, sewage sludge, slaughterhouse waste, etc are mainly biodegradable wastes) and ii) non-biodegradable wastes (Not decomposed by bacteria or other living organisms. Footwear, fibres, metals, different polymeric materials like plastic containers, plastic bags,water bottles and metal cans etc are non-biodegradable wastes) [1-2].

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Fig.-1 shows the different sources of waste which can be identified by recognizing the types of wastes.

Figure 1: Different sources of waste

Pyrolysis, incineration, chemical and thermal treatment, and biological treatment are often used for proper and complete degradation of waste. But often these are accompanied with a lot of challenges starting from technical and logistic difficulties to various environmental pollutions. A small segment of these wastes is recycled and rest ends up in landfills [3-4].

The massive consumption of wide range plastic products has generated a huge amount of plastic waste. There is a need to provide awareness of their uses and routine management as a part of our lifestyle. Nowadays, plastics are increasingly being used in our daily life activities, including the packaging in different food and brewing companies, cosmetics, pharmaceutical, and other production sectors need to pack their end products for efficient and safer product's delivery to the community. Plastics are produced through the process of polymerization or polycondensation of different monomers in general. The post-use of generated plastic waste has many adverse impacts on the environment since these are non-biodegradable wastes if not processed and managed in a proper way [5].

About five billion tons of plastic wastes have accumulated in landfills and the natural environment over the past 50 years. Observing such dreadful impact of plastic pollutions, efforts has been made by different researchers to treat plastic polymers in a green way, i.e.super critical water treatment.

In this review article, we have tried for a comparative study of some important polymers like PET, ABS, PC, HIPS, PP and PS being treated under SCW and their plausible outcomes.

2. Why super critical water (SCW)?

For the recycling of plastics, chemical recycling is the most desirable process because plastics are converted to their monomers, which can then be reused. Sub- and supercritical fluids such as water are excellent reaction media for depolymerisation or decomposition of plastics. A number of researchers were involved in the development of recycling technology from the fundamental to the practical scale. Pilot and commercial scale plants have been constructed for chemical recycling of plastics using sub- and supercritical fluids.[6-8]

3. How does a system of supercritical water equipment work?

Supercritical water is a dense single phase with transport properties similar to those of its vapour phase, and solvent properties comparable to those of a non-polar solvent [9]. Oxygen is fully soluble in supercritical water, resulting in extremely rapid and complete oxidation of all organic compounds to carbon dioxide, clean water (that can be reused), and some non-leachable inorganic salts. Figure 2 represents the temperature range, where water exists under supercritical conditions [10].

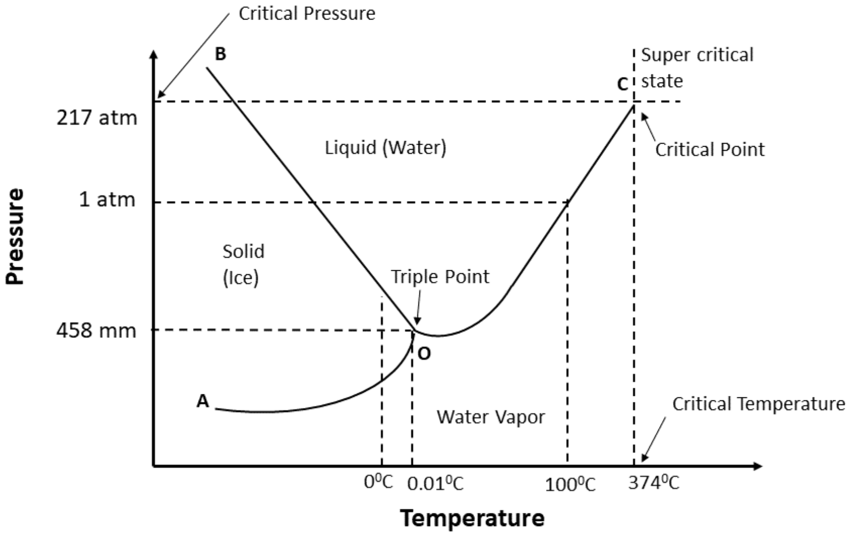


Figure 2: Supercritical phase of water

A supercritical water oxidation system of a homogenous reaction makes use of the unique properties of water at conditions above its thermodynamic critical point, which is at a pressure of 217.7atm and 374.15⁰ C [11-12]. Under these conditions, organic materials, oxidation reactants, and oxidation products are rendered miscible in water, allowing complete oxidation to take place at a high rate. The result of this high temperature and high pressure process is the breakdown of the waste into its monomer, carbon dioxide, water and salts, all of which can be released into the environment or reused for other industrial purposes without any post treatment. Figure 3 represents a basic apparatus outline of an industrial supercritical water oxidation system (iSCWO).

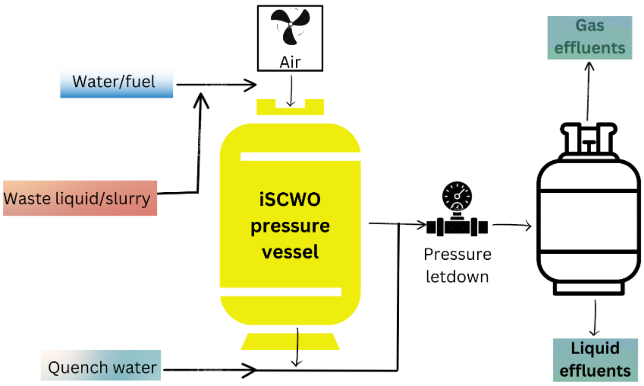


Figure 3: Apparatus outline of Super Critical Water Oxidation system

4. Different polymers possibly treated using SCW

Several scientists and researchers around the world did intensive research works to study the degradation of plastic polymers under super critical water conditions. A different range of polymers were used which yielded several parent monomers with a high yield percentage. Some of such works are tabulated below in Table-1.

Table 1: Different polymers studied at a glance

Plastic polymers used for degradation	**Maximum Temperature giving highest yield (^oC)**	**Highest percentage yield (%)**	**Major monomers/products yielded**	**References**
Polyethylene Terephthalate (PET)	300°C	90%	Terephthalic acid (TPA)	[13]
Acrynonitrile-Butadiene-Styrene (ABS)	400°C	66%	Styrene	[14]
Polycarbonate(PC)	400°C	57.70%	Phenol	[15]
High Intensity Polystyrene (HIPS)	490°C	65.3%	Toluene and ethylbenzene	[16]
Polypropylene (PP)	425°C	95%	Naptha like products	[17]
Polystyrene (PS)	450°C	53%	Methane	[18]

5. Different Polymers under investigation

Under this section, effort has been made to study a little more in details as to how different plastic polymers has been degraded under super critical water conditions over ranges of temperatures and pressures and which among them gave high yield and possible reasons behind it.

A) Polyethylene Terephthalate (PET)

PET is an important commercial polymer with a low price and is one of the most widely used semicrystalline thermoplastic types of plastic resins, with excellent mechanical and thermal properties. Furthermore, a positive feature of PET is that it can be repeatedly recycled, which means a reduction in wasted PET. PET waste can be recycled with four main methods: primary (re-extrusion), secondary (mechanical), tertiary (chemical) and quaternary (energy recovery) recycling [19]. Different depolymerization methods of PET such as glycolysis, methanolysis, ethanolysis and hydrolysis have been studied [20-22].

Waste PET was depolymerized with excess water in absence of catalysts in sub- and supercritical conditions. From a theoretical perspective, if PET degradation was complete, the reaction products consisted of terephthalic acid (TPA) as the main product with ethylene glycol (EG) and water. The reaction pathway of TPA degradation is shown in Figure 4 [23]. In the case of incomplete degradation of PET, the liquid phase was composed mainly of water, ethylene glycol and diethylene glycol, and the solid phase consisted mainly of unreacted PET, oligomers and terephthalic acid. Also, due to the drastic reaction conditions, it was possible the formation of other secondary products such as benzoic acid, 1,4-dioxane, acetaldehyde and crotonic acid [13, 23-25].

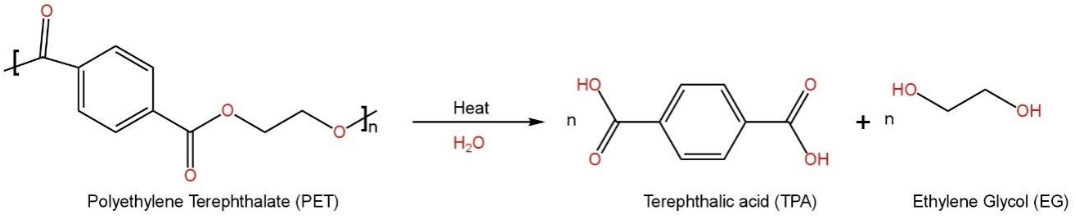


Figure 4: TPA degradation to Terephthalic acid & ethylene glycol

Table 2 shows the experimental data of degradation of PET bottles over ranges of temperatures and time duration at 300 bar pressures [23].

Table 2: Experimental data of degradation of PET bottles [23]

Temperature (°C)	Time (mins)	Yield of TPA (%)
300	30	91.36
300	15	92.92
300	1	93.46
385	30	79.59
385	15	78.27
385	1	84.72

Based on the results of present investigation, which show that a relatively low reaction temperature (3000C) and a short reaction period (1-15 min) was required for production of TPA in high yield (85–90%) and high purity (98%).The fact that similar results were obtained for colourless and green waste and that the method does not produce extensive secondary products that could contaminate industrial and municipal waters, and on an energy consumption analysis, it can be concluded that this method could be very helpful for chemical degradation of PET waste.

However, with prolonging reaction time at these temperatures, the TPA yield followed a decreasing trend in all cases and more degradation products of TPA were produced. Potential pathway of formation of by-products in degradation of PET materials at high temperature and prolonged period is given below in Figure 5.

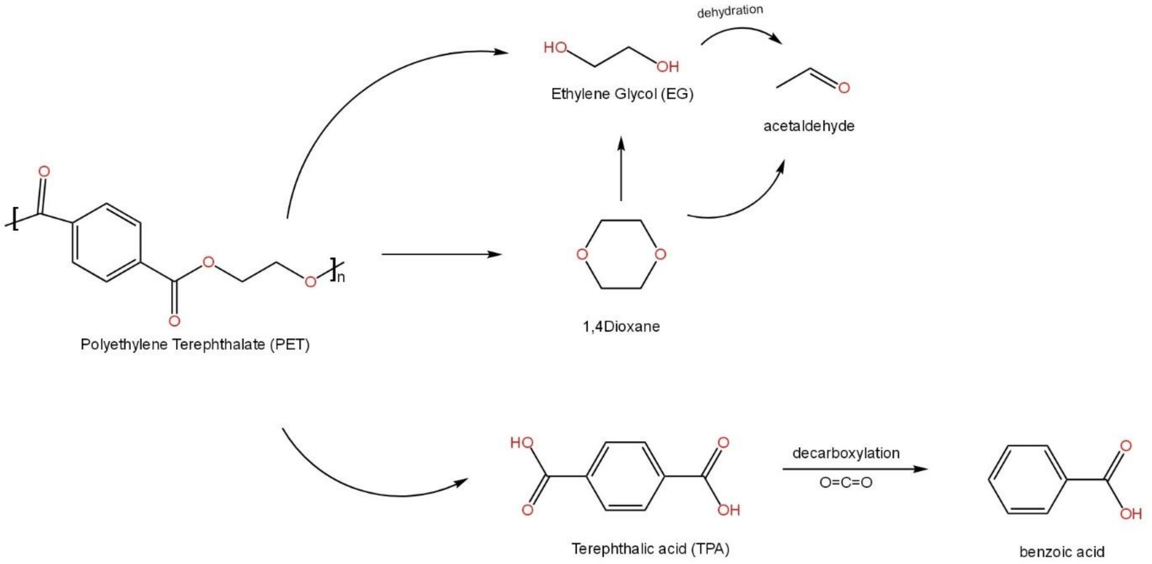


Figure 5: Potential pathways of the degradation of PET waste under supercritical water.

B) Acrylonitrile-Butadiene-Styrene (ABS)polymers

ABS ter-polymers are commonly used to make plastic face guards for wall sockets and protective housing for power tools. It is also commonly used in the automotive field too. ABS plastics are known to have high rigidity, good insulating properties and high impact resistance even at low temperature.

There are mainly two ways for the SCW treatment of plastic wastes. One way is to convert the plastic into hydrogen, methane, carbon monoxide and other hydrocarbon fuel gases to achieve the resource utilization of waste, and the other one is to decompose plastic into corresponding monomers to achieve its recovery and recycling the supercritical water hydrolysis (SCWH) [26] at range of temperatures for oil products [14], and optimal reaction condition for monomer recovery was obtained. Figure 6 represents the structure of ABS ter-polymers formed from three different monomers.

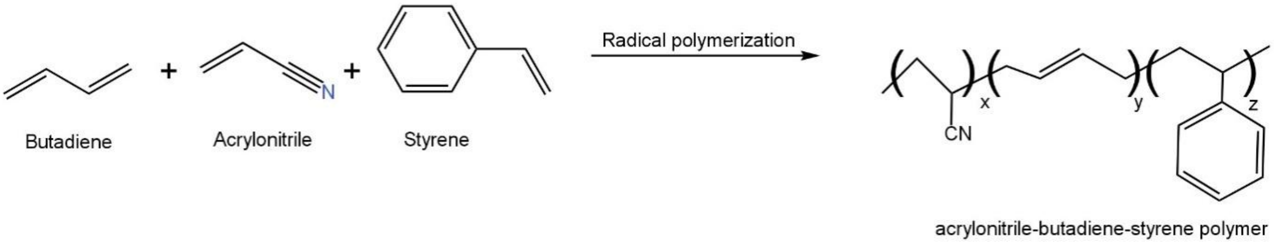
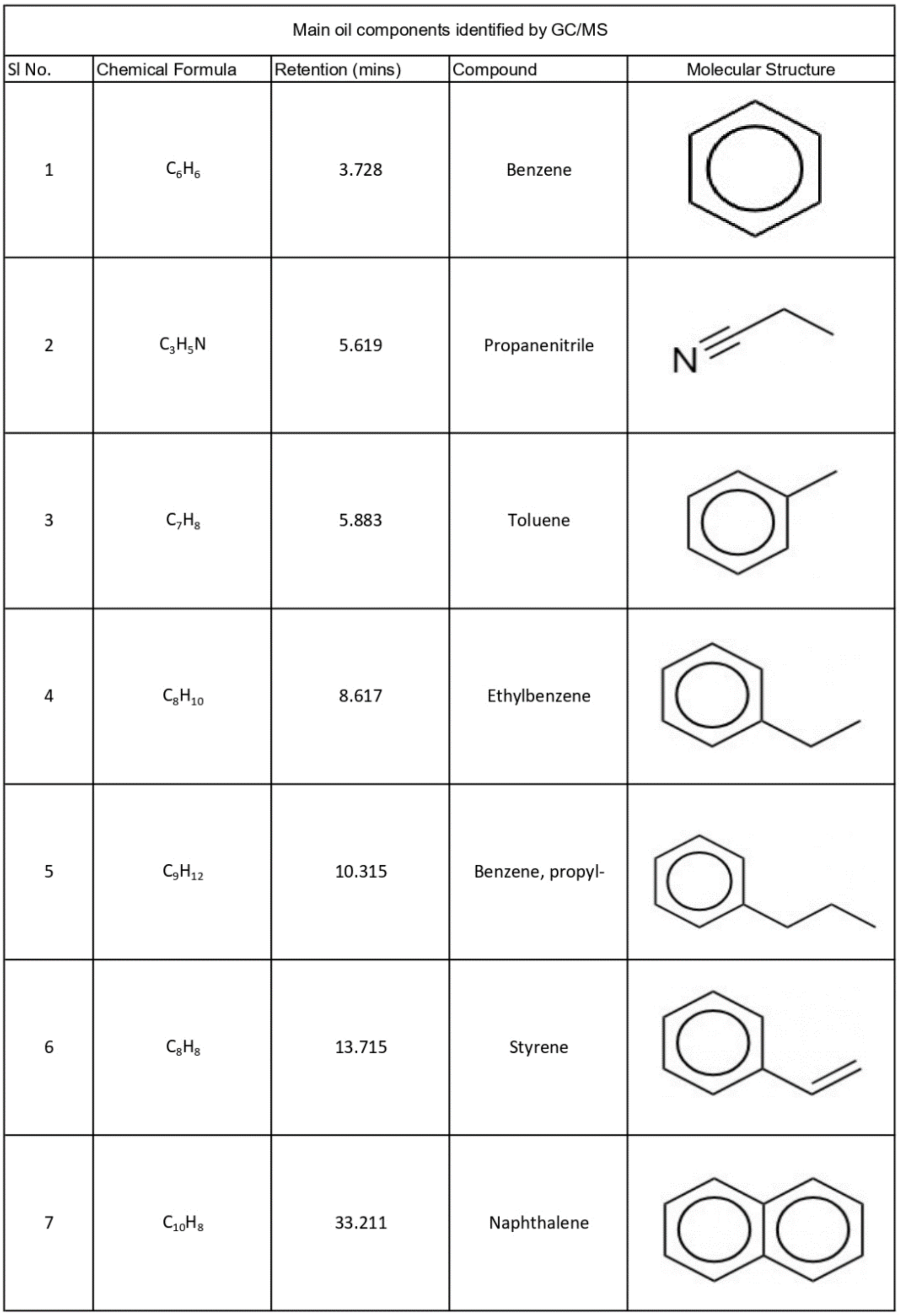


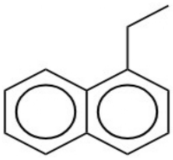
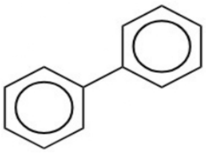
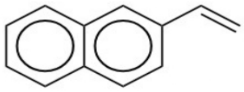
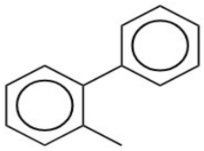
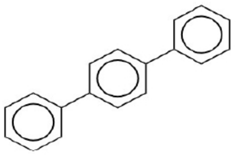
Figure 6: Structure of ABS polymer

The SCWH experiments of ABS polymers were conducted by the scientist at a range of temperatures from 375oC to 450oC, at 21 MPa, for the recovery of oil products [14]. The organic compounds were qualitatively detected by Gas chromatography-mass spectrometry (GC-MS), and Table 3 shows the retention time (it is a measure of the time taken for a solute to pass through a chromatography column) and corresponding molecular structure of each product at 400oC for 60 min [14]. It was observed from the analysis results that, among the three monomers of ABS polymers, only styrene was detected, and the other two monomers acrylonitrile and butadiene were not found in the products. This was because the monomers had high reactivity and were converted into more stable substances in the supercritical water environment, for example, propane nitrile, which was detected in the products, may be produced through the hydrogenation of acrylonitrile.

Table 3: The retention time and corresponding molecular structure of each product from ABS



Main oil components identified by GC/MS				
Sl No.	Chemical Formula	Retention (mins)	Compound	Molecular Structure
1	C_6H_6	3.728	Benzene	
2	C_3H_5N	5.619	Propanenitrile	N
3	C_7H_8	5.883	Toluene	
4	C_8H_{10}	8.617	Ethylbenzene	
5	C_9H_{12}	10.315	Benzene, propyl-	
6	C_8H_8	13.715	Styrene	
7	$C_{10}H_8$	33.211	Naphthalene	

8	$C_{11}H_{10}$	36.755	Naphthalene, 2-methyl-	
9	$C_{12}H_{12}$	38.063	Naphthalene, 1-ethyl-	
10	$C_{12}H_{10}$	39.026	Biphenyl	
11	$C_{12}H_{10}$	41.908	Naphthalene, 2-ethnyl-	
12	$C_{13}H_{12}$	44.348	1,1'-Biphenyl, 2-methyl-	
13	$C_{18}H_{14}$	58.955	p-Terphenyl	

Besides, based on Figure 7 through the comparison of styrene concentrations at different temperatures, the experiments performed at 400oC basically showed the best hydrolysis results, especially at the reaction time of 3 min where the same had been increased by at least 66% and at most 378% compared with other three temperatures [14]. In conclusion, therefore, the optimal SCWH reaction condition for monomer recovery was determined to be 4000C for 3 min in this study.

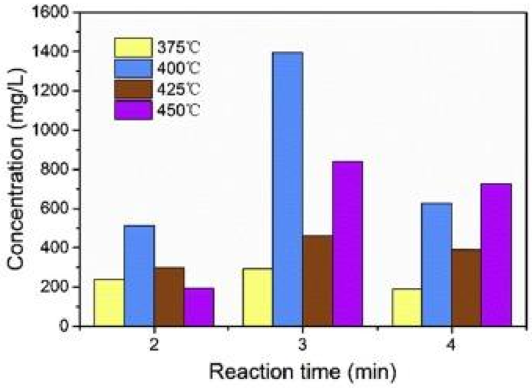


Figure 7: Variation of styrene concentration with reaction time at different temperatures at 21 MPa

C) Polycarbonate (PC)

Nowadays, polycarbonate (PC) has become the fastest-growing polymer due to its excellent properties [27-28]. However, the safety of bisphenol A (BPA) substances contained in PC always is controversial, as some studies have found that BPA can be released from PC products, such as baby bottles and food packaging, which threaten human health [29-31]. So, it is necessary to dispose of waste PC safely and reasonably. Disposal with supercritical water is a good exploration for achieving the green upgradation of PC.

Response relationship between different reaction conditions (temperature 300−500 °C, time 10−60 min, feedstock concentration 5–15 wt %) and CE (carbon liquefaction efficiency of plastics) of PC was established by the scientists, and the results reflected that PC liquefaction favoured mild reaction temperature, long residence time, and low feedstock concentration. Phenol was the largest liquefied product from PC, followed by IPrP (4-isopropenyl phenol) and IPP (4-isopropylphenol), and the recovery efficiency of these three components determined the level of liquefaction efficiency from PC. At 400 °C for 60 min and 5 wt %, the RE(recovery efficiency of identified components) values of phenol, IPP, and IPrP were 29.20, 5.79, and 19.08 wt %, respectively[15]. Figure 8 shows possible liquefaction mechanism of polycarbonate polymers.

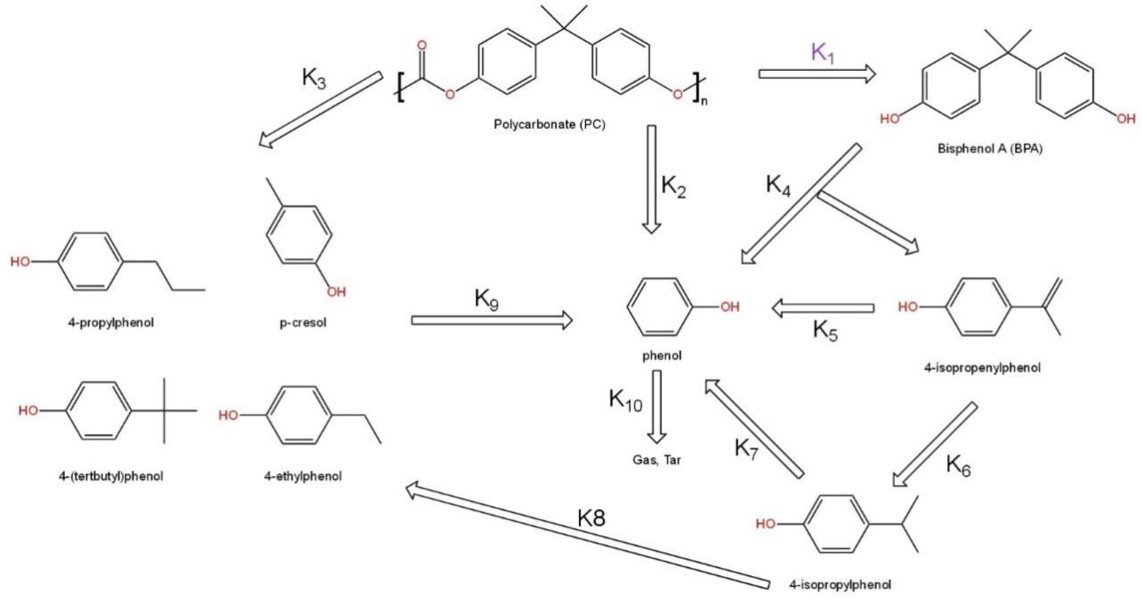


Figure 8: Liquefaction mechanism of PC

D) High Intensity Polystyrene (HIPS)

HIPS are used in printed graphics, shelves and making of models and prototypes of several order. HIPS are known to have good dimensional strength, balanced properties of impact strength and heat resistance [32]. In order to solve the problem of low thermal conductivity and high viscous molten liquid reaction product in the process of plastic liquefaction, the experiments of high impact polystyrene (HIPS) plastic liquefaction were carried out in supercritical water. It was found that the liquid products of HIPS plastic were mainly toluene and ethylbenzene rather than styrene, which was a product of polystyrene. The experimental results showed that plastic first depolymerized to form styrene and 1,3-diphenylpropane, which were then converted to toluene and ethylbenzene. The increase in temperature promoted this transformation process and some traces of polycyclic aromatic hydrocarbons were also produced. At 490oC, the maximum carbon liquefaction rate of 77.0 wt% was obtained, which was 6 times higher than the conventional pyrolysis, and the content of toluene and ethylbenzene were 14wt% and 51.3 wt%, respectively [16]. Figure 9 explains the structure of HIPS polymers.

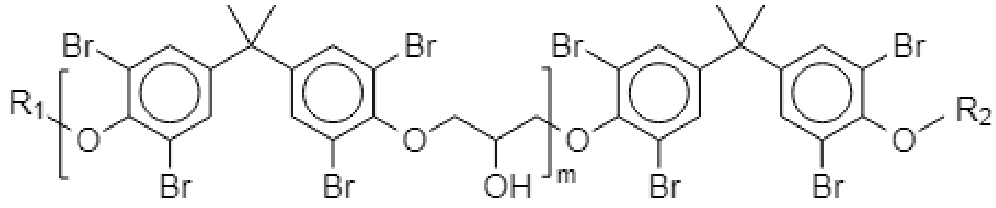


Figure 9: Structure of HIPS polymer

It can be seen from Figure 8 that the plastic liquid product components are mainly differentbenzene ring aromatic compounds. Among them, monocyclic aromatic compounds are toluene, ethylbenzene, isopropylbenzene, styrene and a-methylstyrene, and polycyclic aromatic compounds are naphthalene, biphenyl, 1,3- diphenylpropane, and 2-phenylnaphthalene. [16]

E) Polypropylene (PP)

Polypropylene (PP) have good chemical resistance and translucent properties. They are mainly used for the preparation of ropes, tapes and carpets. Polypropylene (PP) waste accounts for about 23% of the total plastic waste [33]. Converting PP waste into useful products can reduce theaccumulated waste and associated risks to the environment and human health. In general, model PP was converted into oil using supercritical water at 380-500°C and 23 MPa over a reaction time of 0.5-6 hr. Up to 91wt.% of model PP was converted into oil at 425°C with a 2-4 h reaction time or at 450°C with a 0.5-1 h reaction time. Higher reaction temperatures (>450°C) or longer reaction times (>4 hr) ledto more gas products. The oil products consisted of olefins, paraffins, cyclics, and aromatics compounds. About80-90 wt% of the oil components had the same boiling point range as naphtha (25-200°C) and heating values of 48-49 MJ/kg.

Based on the analyses of the products in different phases under a range of reaction times and temperatures, potential reaction pathways of major intermediates in the conversion of PP are summarized in Figure 10 [17]. During the same time, small amounts of unsaturated aliphatics(olefins) may converted to saturated aliphatics (paraffins) and aromatics. Theoretically, aromatization can occur by either dehydrogenation of cyclics or cyclotrimerization of unsaturated aliphatics (olefins) [34-35].

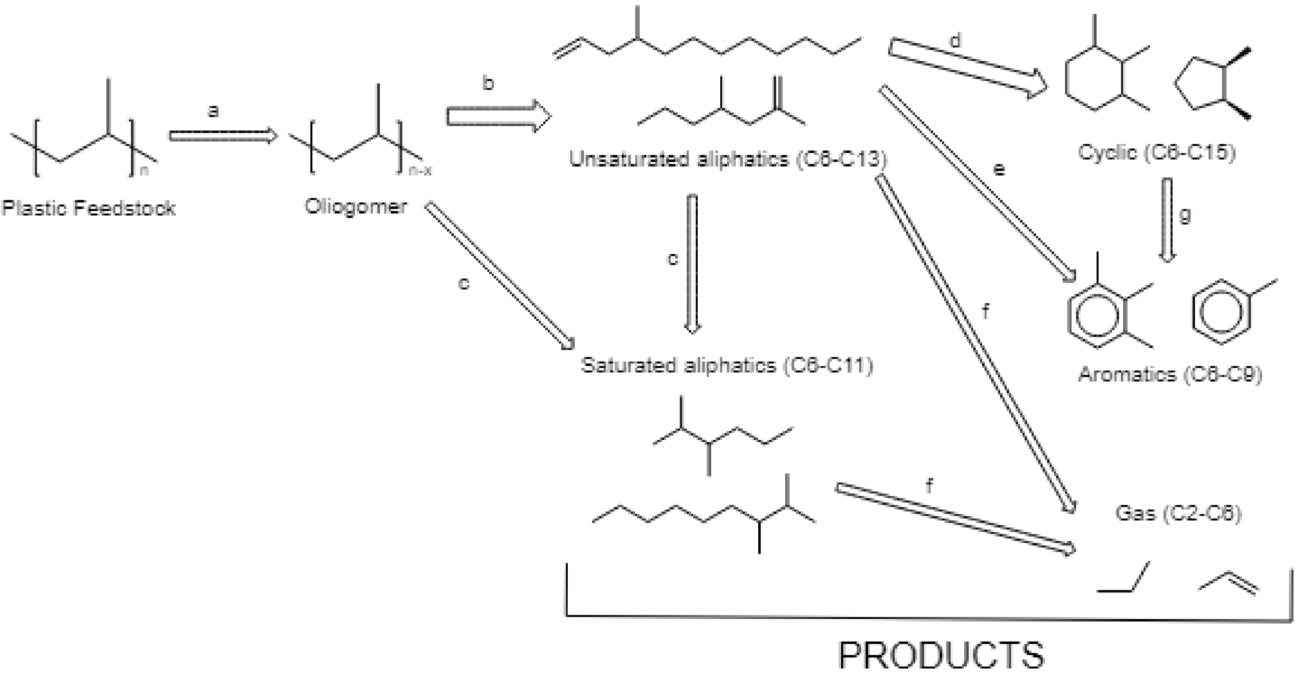
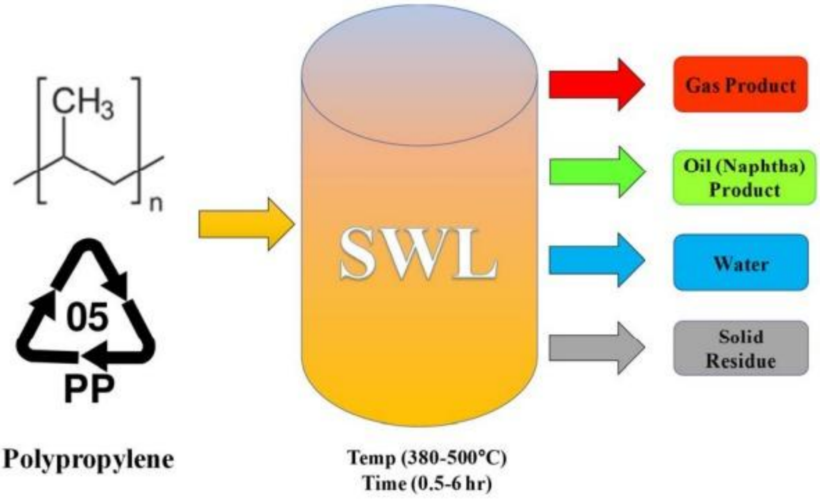


Figure 10: A potential reaction scheme of converting PP via SWL: (a) depolymerization, (b) cracking, (c) hydrogenation/saturation, (d) cyclization, (e) aromatization, (f) gasification, and (g) dehydrogenation



Conversion of polypropylene (PP) into naphtha using supercritical water liquefaction (SWL).

F) Polystyrene (PS)

Polystyrene is hard, stiff, transparent synthetic resin mostly used in food service industries as foam cups and bowls, rigid trays and containers [36]. Detailed catalytic mechanisms of RuO2 during supercritical water gasification of common polyolefin plastics including polystyrene (PP) have been investigated in a batch reactor at 450o C for 60min [18]. Evaluation of the gas yields, CGE (carbon gasification efficiency) and HE (hydrogen gasification efficiency) revealed that the conversion of PS involved thermal degradation, steam reforming and methanation, whereas hydrogenolysis was a possible additional mechanism during the conversion of aliphatic plastics. The process has the benefits of producing a clean-pressurized methane-rich fuel gas as well as cleaning up hydrocarbons-polluted waters. Figure 11 displays the structure of Polystyrene.

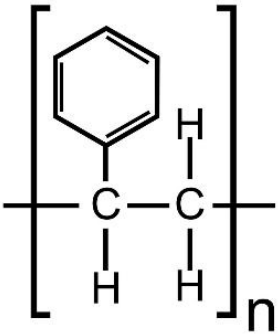
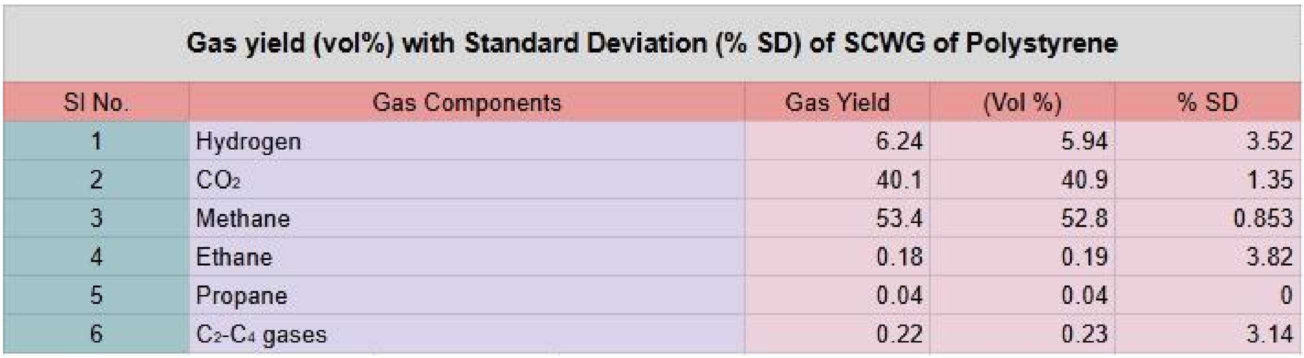


Figure 11: Structure of Polystyrene

This present study had provided some insights into the catalytic SCWG of common olefin plastics like polystyrene in the presence of RuO2-based catalysts to produce methane [18]. An attempt was made to understand and explain the reaction mechanisms responsible for the yields of gas products during this process. The table 4 below displays different gas produced from PS after degradation.

Table 4: Different gas produced from PS after degradation [18]



Gas yield (vol%) with Standard Deviation (% SD) of SCWG of Polystyrene

Sl No.	Gas Components	Gas Yield	(Vol %)	% SD
1	Hydrogen	6.24	5.94	3.52
2	CO_2	40.1	40.9	1.35
3	Methane	53.4	52.8	0.853
4	Ethane	0.18	0.19	3.82
5	Propane	0.04	0.04	0
6	C_2-C_4 gases	0.22	0.23	3.14

6. Conclusion

In this study above, the degradation in terms of liquefaction and gastification of plastic using supercritical water was a good way to recycle plastic waste, which is also the prerequisite for the efficient breakdown of plastic waste. Each plastic has its own different degradation behaviour, and no universal solution provides an optimum for each plastic in a mixture. During the liquefaction and gastification process of plastics, complex andvariable interactions occur between different monomers, causingchanges in the desired product fuel and monomers. In some cases, a prolonged duration of heating yielded high products whereas a very short duration was enough to give efficient yields in some cases. Hopefully, more detailed studies will be done in this field and very soon industries adopt these methods and commercialise it.The major challenge faced by the use of supercritical water for the degradation of plastics is the high logistics involved in buying and maintaining the SCW apparatus. Along with that, the energy requirement to maintain a constant high temperature and pressure is also one of the major common challenges faced by all the researchers.

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