

Depolymerization of Polypropylene Plastic Wastes under Solvothermal Liquefaction  
Conditions

by

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## ABSTRACT

Polypropylene, a non-biodegradable plastic with a higher **c-c** bond disassociation energy than other conventional polymers like Polyethylene (PE), is used to manufacture these three-layered masks. The amount of plastic pollution in the environment has grown tremendously, nearing million tons in a short period of time. As a result, the purpose of this study is to reduce the environmental damage caused by facemasks.

This M.S. thesis offers a concise overview of various thermochemical methods employed to depolymerize plastic waste materials. It emphasizes environmentally conscious and sustainable practices, specifically focusing on solvothermal processing. This innovative approach aims to convert discarded face masks into valuable resources, including hydrocarbons suitable for jet fuel and other useful products.

The thesis provides an in-depth exploration of experimental investigations into solvothermal liquefaction techniques. Operating under specific conditions, namely, a temperature of 350°C and a reaction duration of 90 minutes, the results were notably impressive. These results included an exceptional conversion rate of 99.8%, an oil yield of 39.3%, and higher heating values (HHV) of 46.81 MJ/kg for the generated oil samples. It's worth noting that the HHV of the oil samples obtained through the solvothermal liquefaction (STL) method, at 46.82 MJ/kg, surpasses the HHV of gasoline, which stands at 43.4 MJ/kg.

The significant role of the solvent in the depolymerization process involves the dissolution and dispersion of the feedstock through solvation. This reduces the required thermal cracking temperature by enhancing mass and thermal energy transfer. While solvolysis reactions between the solvent and feedstock are limited in thermal liquefaction, the primary depolymerization process follows thermal cracking. This involves the random scission of polypropylene (PP) molecules during heat treatment, with minimal polymerization, cyclization, and radical recombination reactions occurring through free radical mechanisms.

Overall, this work demonstrates the feasibility of a highly promising technique for the effective chemical upcycling of polypropylene-based plastics into valuable resources, particularly in the context of jet fuel hydrocarbons, showcasing the comprehensive analytical methods employed to characterize the products of this innovative process.

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## CHAPTER

### 1. INTRODUCTION

#### 1.1 Problem Statement

Humans are becoming more conscious of what they eat and whom they associate with in order to protect themselves against deadly viruses like Corona. Several medicines and vaccinations have been made available on the open market to protect humans[1]. However, the constant emergence of new viruses has made it challenging to produce new medications and vaccines. Additionally, side effects caused by commonly used drugs on the hematopoietic system and the cardiovascular system and other organs[2] made it more difficult to trust these medications and vaccines. As a result, people are more inclined towards using personal protection equipment (PPE) to protect themselves while also preventing the spreading airborne diseases[3], [4]. Face masks are in high demand these days because of their easy availability while also being cost-effective. However, these face masks are made of polypropylene polymers, a non-biodegradable plastic with higher thermal stability than typical polyethylene, making the decomposition conditions more difficult[5] and due to the lack of adequate disposal techniques, their plastics are stacking up in the environment, causing major microplastic pollution[6], [7]. According to studies, million tons of mask pollution have surged in the last two years[8] and the production rate of polypropylene is around 55 million tons per year [9], [10].



*Fig (1): PPE Waste [11].*

## 1.2 Current Status

Conventionally 75 % of the plastics produced from 2018 ended up in landfills[12], [13]. The microplastic surface of PP leads to the contamination of air and soil around the landfills [14]. Therefore, recycling PP using the landfills method is not a good option as it takes a lot of space, and longer time as well as pollutes the environment. Mechanical methods like simple mechanical pulverization can be used to convert waste PP into molding products at higher manufacturing efficiency and at lower cost[15]. However, Molded products have low performance and low economic value as the number of recycling increases, the properties of the PP decrease each time, and once it reaches a recycling limit, it can no longer be recycled in the future. Therefore, there is the need to think of the latest advancements or new methods that can completely convert the PP into a useful product and at the same time generate an energy source that can help towards sustainable growth. Chemical recycling methods like (gasification, pyrolysis, hygrothermal liquefaction and solvothermal liquefaction) are the best way to reduce PP plastic waste at the same time generating energy.

Xiao et al [15] employed a gasification technique for the conversion of polypropylene (PP) plastic, achieving the highest yield with approximately 85% syngas, 5% tar, and 10% char. While gasification generates syngas, a valuable resource for fuel and chemical production through established processes [16], the economic viability is hindered by the fact that syngas is not inherently profitable. Simultaneously, the generated tar and char are considered waste products. Consequently, gasification may not be considered an economically feasible option for the depolymerization of polypropylene (PP). Pyrolysis is one of the latest technologies that can depolymerize PP plastic waste. Parku et al[16] reported the highest 97.5% conversion of PP at 600 °C. However, out of 97.5% conversion, 68.6% is heavy oil fraction and only 13.8% is light oil fraction and other studies have also reported that the pyrolysis of plastic produces denser, chemicals and gases [17], [18]. Therefore, the pyrolysis of PP plastic uses higher energy input and produces heavy oil fraction with negligible gas yield.

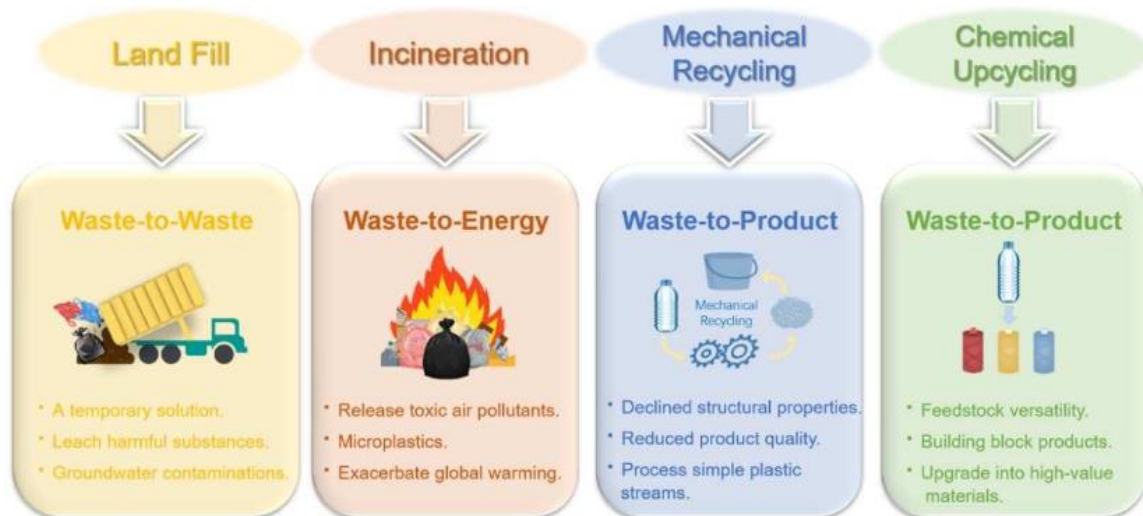


Fig (2): Overview of Different Plastic Recycling Methods[11]

Hydrothermal liquefaction (HTL) is an emerging technology used very widely in the valorization of biomass and used in plastic waste to generate energy and other chemical products [19]– [21]. Seshasayee & Savage [22] reported that approximately 17% of crude oil was extracted from PP at 450 c and 30 min reaction time in supercritical water. Hence, the thermal liquefaction of polypropylene (PP) utilizing water as a solvent exhibits minimal conversion, resulting in meager oil and gas yields. [23] and HTL of PP is not economically viable for the industries due to its high energy input of higher temperature and high pressures.

Researchers introduced adding solvents like acetone, methanol, and some other organic solvents to HTL and replaced water. Methanol and acetone show excellent solvent properties and are used in recovering energy from various plastic waste [21], [24]– [28]. Solvents have a lower critical temperature and pressure making them easier to operate and found to increase oil and gas yields at lower reaction temperatures [29]. A fair amount of work has been done on the different solvents but not hexane and heptane. Additionally, both hexane and heptane are often used to extract oil from seeds and plants [30]. Although solvothermal liquefaction (STL) shows excellent polymer degradation performance and the variety of organic solvents provides great selectivity, the polarity and functional groups of the solvents are many, leading to diverse reaction mechanisms. However, only very limited cases were reported, so the STL technology and various solvent reaction mechanisms remain to be further investigated and improved.

### 1.3 Proposed Solution

Depolymerization of polypropylene is a challenging task in chemical recycling because the C – C bond breakage in PP is only possible at very high temperatures. In this study, we have examined the components present in the oil products of PP-facemasks plastic waste, and the effects of temperature and residence time on the depolymerization reactions focusing on the exploration of the process and pathway of thermal liquefaction reaction in hexane and heptane solvent systems, to overcome the technical obstacles of PP energy conversion. The work provides the theoretical basis for the improvement of STL technology and the commercialization of facemasks plastic upcycling and valorization.

## 2. LITERATURE REVIEW

### 2.1 Pyrolysis

Pyrolysis is defined as the thermal degradation of organic materials in the absence of oxygen, induced by heat. In the context of plastic waste management, plastic pyrolysis occurs within a temperature range of 250°C to 900°C, devoid of oxygen, resulting in the production of liquid oil. This process involves feeding plastic materials into a reactor, where heat transfer facilitates the conversion of plastics into liquid oil. Subsequently, the char residue is separated and filtered from the oil, allowing for the condensation and cooling of the liquid oil, rendering it suitable for storage and future utilization.

Pyrolysis methods can be categorized into three types: slow, intermediate, and fast pyrolysis, each distinguished by varying heating rates and process characteristics. Slow pyrolysis, characterized by lower heating rates and extended residence times, is favored when seeking lower oil yields. Intermediate pyrolysis operates at temperatures typically between 300°C and 500°C, making it suitable for producing products with lower viscosity properties. Fast pyrolysis, the preferred method when liquid oil is the desired end product, involves rapid polymer decomposition into vapors, which are promptly condensed to liquid form, minimizing the risk of secondary decomposition. Fast pyrolysis primarily yields higher amounts of liquid oil and gaseous products.

In addition to conventional pyrolysis techniques, catalytic pyrolysis is employed to mitigate reaction challenges and enhance the productivity and selectivity of target products [31]. However, it is worth noting that pyrolysis techniques have certain drawbacks,



including lower conversion rates, limited thermal stability, and the need for meticulous design and operation. Furthermore, the plastic oil obtained through pyrolysis typically presents as a brown, viscous liquid, primarily comprising aromatic compounds. To meet practical application standards, further upgrading and reforming of these components are necessary[32], [33].

*Table (1): Summary of Key Studies on Converting PP Plastic Using Pyrolysis.*

Plastic type	Reactor	Catalyst	Conditions	Yields [wt %]			Ref
				Gas	Liquid	Solid	
PP	Two fixed beds	Fe/Al <sub>2</sub> O <sub>3</sub>	800°C	43.4	26.1	30.5	[34]
PP	Two stage reactors	HZSM-5; NiO	750°C	56.1	9.6	34.3	[34]
PP	Fixed bed	AC mixed with Ni <sub>2</sub> O <sub>3</sub> , Co <sub>2</sub> O <sub>3</sub> , and Fe <sub>2</sub> O <sub>3</sub>	820°C	42.8	8.7	48.5	[35]
PP	Two fixed beds	Fe-Ni	800°C	48.6	20	31.4	[36]

Table (1) presents a comprehensive overview of pyrolysis experiments aimed at degrading polypropylene (PP) plastic, highlighting various reactor configurations, catalysts, and operating conditions. Pyrolysis, as depicted, is conducted at notably high temperatures, emphasizing the thermal intensity of this waste plastic conversion process. To optimize the product outcome, a diverse range of catalysts, such as Fe/Al<sub>2</sub>O<sub>3</sub>, HZSM-5, NiO, AC mixed with Ni<sub>2</sub>O<sub>3</sub>, Co<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub>, and Fe-Ni, and many more have been employed. The results

demonstrate a spectrum of yields, with variations in gas, liquid, and solid products. Notably, the pyrolysis of PP seems to yield a relatively low conversion rate, with varied distributions of products. These findings underscore the complexity of PP degradation through pyrolysis and the significance of catalyst selection and operational conditions in achieving desired product outcomes. Further investigation and optimization may hold the key to enhancing the efficiency of PP waste conversion via pyrolytic methods.

## 2.2 Gasification

Gasification is a highly versatile conversion technology that plays a pivotal role in transforming carbon-containing materials, including plastics, into a valuable resource known as synthesis gas or syngas. Unlike combustion, gasification is a multi-step process involving the partial oxidation of plastic waste at extremely high temperatures within a gasification medium.

In the gasification process, plastic waste undergoes a controlled reaction with a gasifying agent, such as steam, oxygen, or air, typically at temperatures ranging from 500°C to 1300°C. This reaction generates syngas as its primary output. Syngas, comprising hydrogen and carbon monoxide, have significant potential for various applications, including the production of renewable fuels and chemicals. Key advantages of gasification include , high efficiency Gasification systems boast remarkable efficiency compared to other renewable energy sources like wind and solar power. Syngas Conversion to harness the full potential of syngas, an auxiliary process, such as Fischer-Tropsch synthesis[37], can be employed to convert syngas into valuable fuels and chemicals.

Gasifiers are highly adaptable and can be customized based on factors like fuel availability, shape, size, moisture content, and ash content. They are broadly categorized into two types: fixed bed and fluidized bed gasifiers. Further classification includes downdraft, updraft, and cross-draft gasifiers, depending on the gasifying agents employed.

However, it is important to acknowledge the complexity and sensitivity of the gasification process. Gasification typically requires a significant start-up time, often exceeding half an hour, and achieving the desired state of producer gas can be challenging. One of the byproducts of gasification is tar, which necessitates careful management.

Strict requirements for fuel characteristics, such as size, moisture content, and ash content, are imposed by all gasifiers. Inadequate fuel preparation can lead to technical complications in gasification processes. To enhance the sustainability of plastic depolymerization via gasification, ongoing research is exploring various avenues, including the incorporation of heat recovery devices, improved methods for tar cracking, the reuse of solid residue as feedstock, the transformation of ash and tar into value-added products, and steam gasification to maximize hydrogen yield. It's worth noting that while gasification offers promise, it can be capital-intensive, and ongoing research efforts are essential to optimize its efficiency and environmental impact in the context of plastic waste management.

Table (2): Summary of key Studies on Converting PP Plastic Using Gasification.

Plastic type	Reactor	catalyst	Conditions	Gas compositions [vol%]				H2 yield mmol/g	Ref
				H <sub>2</sub>	CH <sub>4</sub>	CO	CO <sub>2</sub>		
PP	Spouted bed + fluidized bed	Ni/CeO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	700°C	77.8	1.4	14.3	51.2	166.8	[38]
PP	Spouted bed + fluidized bed	Ni/La <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub>	700°C	86.0	0.3	34.4	64.0	172.7	[38]
PP	Two fixed beds	Ru/Al <sub>2</sub> O <sub>3</sub>	680°C	70	1.4	11	16	36.5	[39]

Table (2) provides valuable insights into the gas composition and hydrogen (H<sub>2</sub>) yield resulting from the pyrolysis of polypropylene (PP) plastic under various reactor configurations and catalysts, each operating at different conditions. Notably, the focus here is on the production of hydrogen, a valuable energy carrier, from the gasification of PP.

Despite the promising results, it is important to acknowledge certain drawbacks in these experiments. First, high operating temperatures, such as 700°C and 680°C, may necessitate

significant energy input, potentially making the process less energy efficient. Additionally, the presence of CO<sub>2</sub> in the gas composition indicates that a portion of the carbon content from the plastic is being converted into a less desirable byproduct rather than into H<sub>2</sub>. Therefore, further optimization of the process conditions and catalyst selection may be required to maximize H<sub>2</sub> yield and minimize energy consumption and unwanted byproducts in the gasification of PP plastic.

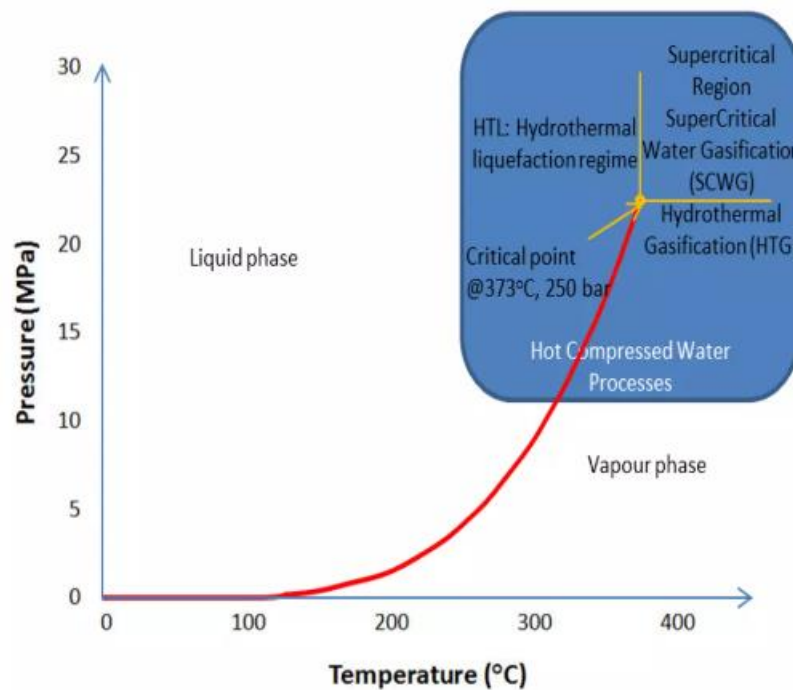
### 2.3 Hydrothermal Liquefaction

Hydrothermal Liquefaction (HTL) stands out as a thermochemical depolymerization process conducted within a sealed reactor. This innovative method facilitates the conversion of diverse feedstocks, such as biomass or plastic waste, into crude oil under critical operating conditions of elevated temperatures (250-400 °C) and pressures (10-25 MPa). HTL generates several key products, including crude oil, solid residue, an aqueous phase, and a gas phase.

The advantages of employing HTL over alternative thermochemical techniques are compelling[40]:

1. Elimination of Feed Drying: Unlike some processes, HTL eliminates the need for pre-drying of feedstock, making it suitable for various plastics.
2. High Carbon Efficiency: HTL boasts an impressive carbon efficiency exceeding 95% during the upgrading step.
3. Aqueous Byproduct Recycling: HTL allows for the recycling of the aqueous byproduct, enhancing resource utilization and minimizing waste.

4. Compact Footprint: HTL's infrastructure has a smaller footprint compared to other thermochemical conversion methods, contributing to space efficiency.
5. Robust and Non-Biological: The HTL process is robust and non-biological in nature, offering stability and reliability.



*Fig (3): Phase Diagram of Water: Supercritical Water Is Beyond the Critical Point, While Subcritical Water Is in the Compressible Liquid State.[41]*

The fuel produced through HTL exhibits superior characteristics when compared to oil obtained from pyrolysis. HTL-derived oil possesses a higher Heating Higher Value (HHV), lower nitrogen content, and lower oxygen content. The high pressure and temperature

conditions of HTL result in a reduced dielectric constant and water density, rendering water less polar and enabling the dissolution of organic compounds under HTL conditions[42]. Compared to pyrolysis, HTL products contain lower levels of oxygen and moisture and exhibit a higher heating value. One of the most significant benefits of HTL is its capability to treat wet waste, including unsorted mixed organic plastics contaminated with minimal energy requirements, eliminating the need for a sorting step.

*Table (3): Summary of key Studies on Converting PP Plastic Using HTL.*

Plastic type	Reaction Conditions			Solid content [wt %]	Plastic/ water	Conversion %	Major oil products	ref
	Temperature	Pressure	Time					
PP	450°C	2 MPa	45 min	8	1:2	87	C4-C25	[43]
PP	380–500°C	23 MPa	0.5–6h	3	1:4	91	Hydrocarbons phenols naphtha	[44]
PP	380–400°C	25 MPa	5–60 min	5	1:6	91	Diesel and lubricant	[45]
PP+pistachio hull	350°C	4.5-10 MPa	1 h	3	1:10	52	Alkanes Carboxylic acid ketones	[46]

However, it's important to note that one industrial challenge associated with HTL is ensuring process safety, particularly concerning the thermal and mechanical stresses placed on the reactor due to the high-pressure, high-temperature environment. Addressing this issue necessitates the careful selection of reactor materials and consideration of the diameter-to-thickness ratio following the operating pressure and the tensile strength of materials at the specified operating temperature [42]. The use of water as a solvent in HTL accounts for the requirement of higher temperatures and pressures, as water exhibits greater critical temperature and pressure compared to other organic solvents.

The presented table (3) highlights key findings related to the hydrothermal liquefaction (HTL) of polypropylene (PP) plastic. Various reaction conditions, including temperature, pressure, and reaction time, were investigated to assess the conversion efficiency and the major composition of the resulting oil products. The table illustrates the potential of HTL as a method for degrading PP plastic, with some notable advantages and challenges.

In these HTL experiments, it is evident that PP plastic can be efficiently converted, with conversion rates as high as 87%. This underscores the effectiveness of HTL in breaking down the polymer structure of PP. However, a closer look at the major oil products generated reveals a predominance of heavy oil products, such as naphtha, and lubricant components. While these products have value, their heaviness poses challenges in terms of usability and downstream processing.

One limitation of HTL is the necessity for energy-intensive separation processes to extract the oil phase from the water mixture. This separation step can be resource-intensive and



may require further optimization to enhance the overall efficiency of the HTL process. Additionally, efforts to fine-tune the HTL conditions and catalysts may hold the potential for increasing the yield of more valuable and lighter oil products, thus improving the overall sustainability and economic viability of PP plastic degradation via HTL.

In summary, the results presented in the table (3) signify the promise of HTL as a method for PP plastic degradation, yet they also point to opportunities for further research and development to optimize product yields and reduce energy-intensive separation steps in the quest for more sustainable and efficient plastic waste conversion.

#### 2.4 Solvothermal Liquefaction

Solvent Thermal Liquefaction (STL) closely resembles HTL, with the key distinction being the substitution of water with various organic solvents. This strategic modification enhances the solvent properties within the HTL system, leading to notable reductions in liquefaction temperatures and pressures required for plastic conversion. Consequently, the introduction of organic solvents represents a significant optimization strategy for the HTL process.

The thermal degradation of polymers within a solvent medium hinges on three pivotal factors, each playing a crucial role in the overall process:

1. Solvation Capacity of the Solvent: The solvent's ability to dissolve and interact with polymer molecules is a pivotal determinant of the liquefaction process's efficiency.

2. Dipole Moment: The dipole moment of a solvent signifies its polarity and influences the dissociation of polymer chains. Higher dipole moments tend to yield higher conversion rates, as they foster more effective interactions with the polymer matrix.

3. Dielectric Constant: The dielectric constant of a solvent impacts its ability to facilitate the flow of electric charges within the system. This property, in turn, influences the overall liquefaction process.

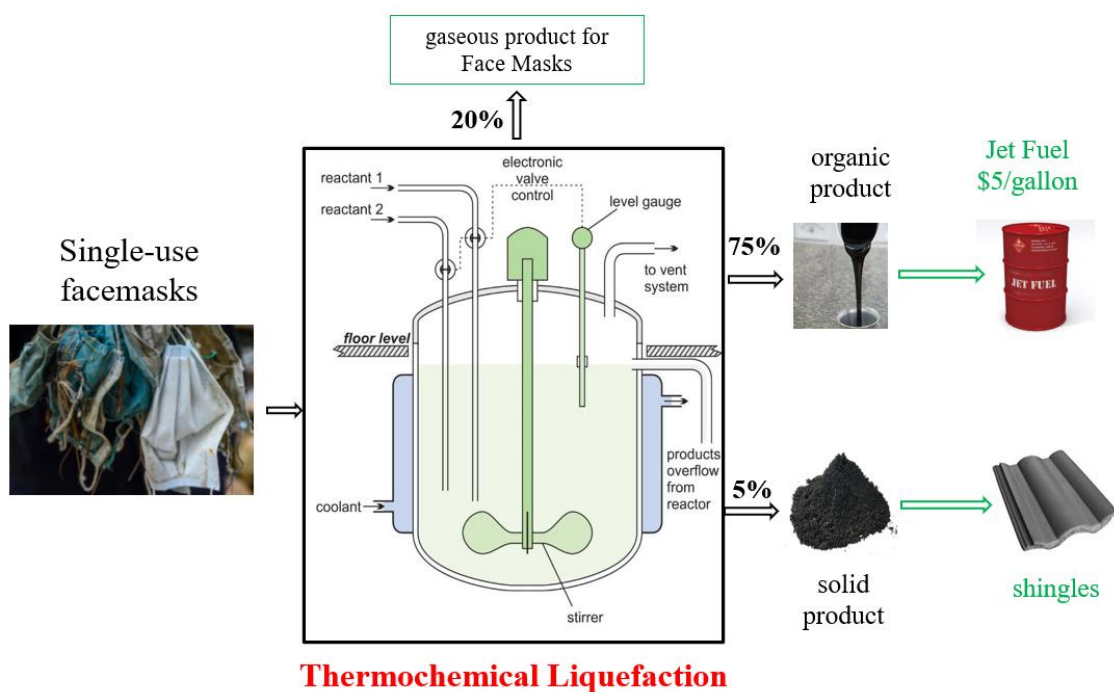
Research findings have demonstrated a direct correlation between the dipole moment of solvents and the conversion rates of polymers. Notably, studies have shown that solvents such as water, methanol, and acetone exhibit varying dipole moments, with acetone possessing the highest and water the lowest[33]. Consequently, these differences in dipole moments translate into distinct conversion rates, with acetone yielding the highest conversion rates and water, the lowest.

These insights underscore the critical role of solvent selectivity within the STL process. The judicious choice of a solvent tailored to the specific feedstock is paramount. This selectivity not only results in enhanced conversion rates but also enables the achievement of these outcomes at lower operating conditions, reducing energy demands and operational costs. Furthermore, the judicious selection of solvents contributes to the production of higher-quality oils with desirable compositions.

*Table (4): Comparison Between Different Thermochemical Methods.*

<b>Thermochemical Methods</b>	<b>Operating Conditions</b>	<b>Advantages</b>	<b>Disadvantages</b>
Gasification	500 – 1300°C	- Efficient energy recovery and syngas generation.	- Intensive syngas purification, tar formation, and elevated operational expenses.
Pyrolysis	250 – 900 °C	Bio-oil and fuel gas are produced.	- Bio-oil necessitates additional refining for direct use and exhibits limited conversion.
Hydrothermal liquefaction	250 – 400 °C 10-25 MPa	- Good conversion rates, Cost-effective	- Bio-oil requires separation from the aqueous phase.
Solvothermal liquefaction	250 – 350 °C < 9 MPa	- Highest conversion rates. - Almost zero residue. - No further separation is needed for bio-oil.	- The operational cost is contingent upon the choice of solvent.

In summary, Solvent Thermal Liquefaction (STL) presents a promising avenue for the efficient conversion of plastic waste. By leveraging the solvent's solvation capacity, dipole moment, and dielectric constant, coupled with meticulous solvent selection, STL optimally enhances the conversion process, making it more energy-efficient and yielding superior oil compositions.



*Fig (4): Overview of Solvothermal Thermal Liquefaction.*

### 3. EXPERIMENTAL SETUP

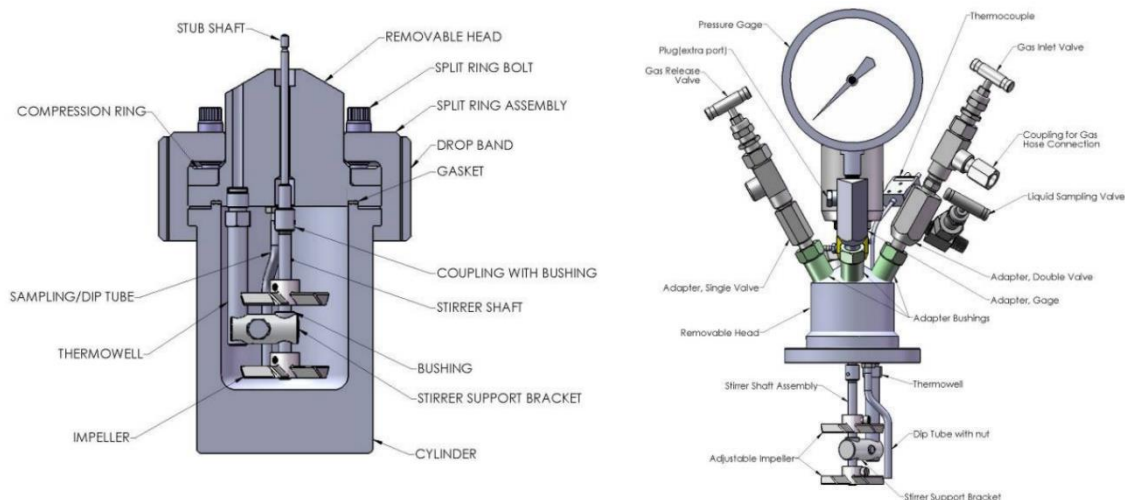
#### 3.1 HTL Reactor

The reactor employed in these experimental studies is a robust stainless-steel vessel, specifically the Model 4593 reactor, manufactured by Parr Instrument Company in Moline, IL. This reactor setup is well-suited for conducting various processes, including Solvent Thermal Liquefaction (STL), owing to its exceptional capabilities and precise control features.

Key attributes of the Parr Model 4593 reactor and its setup include:

1. **Reactor Volume:** The reactor boasts an inner volume of 100 ml, providing ample space for accommodating reactants and facilitating chemical transformations.
2. **Mechanical Stirrer:** To ensure thorough mixing and homogenization of reactants, the setup is equipped with a mechanical stirrer. This component plays a crucial role in promoting efficient reactions by preventing the formation of concentration gradients within the reactor.
3. **Electric Heater:** Temperature control is paramount in many chemical processes, and this reactor is equipped with an electric heater. The temperature is precisely regulated by a 4843 controller, allowing for accurate adjustments to match the desired reaction conditions.
4. **High-Pressure Capabilities:** One of the standout features of the Parr Model 4593 reactor is its capacity to withstand high pressures. It can accommodate pressures of up to 5000 psi, which is particularly well-suited for the rigorous demands of STL studies.

In a batch reactor configuration, reactants are introduced into the reactor vessel, which is then operated under the desired conditions until the target conversion or reaction endpoint is achieved.



*Fig (5): Cross Sectional View of Parr Reactor.*



*Fig (6): Parr Reactor.*

Batch reactors are commonly used in chemical and biochemical processes. They typically consist of tanks or vessels equipped with impellers for stirring and mixing purposes. External heaters, such as the electric heater in this setup, are employed to maintain or adjust the temperature as needed. Additionally, batch reactors are sealed to contain the required pressure levels, which is especially important for high-pressure processes like those encountered in STL studies.

The Parr reactor is further enhanced with instrumentation, including a pressure gauge and a thermocouple. These components offer real-time monitoring of pressure and temperature within the reactor. The data from the thermocouple is also transmitted to the 4843 controller, allowing for precise control and regulation of reaction conditions. This level of instrumentation ensures that experiments can be conducted with a high degree of accuracy and repeatability.

The Parr Model 4593 stainless steel reactor setup is an essential tool for conducting controlled experiments, particularly in the context of STL studies. Its robust construction, precise temperature control, high-pressure capabilities, and real-time monitoring instrumentation make it an invaluable asset in the field of chemical research and process development.

### 3.2 Rotary Evaporator

The rotary evaporator, often referred to as a "rotovap," is a sophisticated and indispensable piece of laboratory equipment widely employed for the precise removal of solvents from various liquid samples, particularly in applications like Solvent Thermal Liquefaction (STL). It operates on the fundamental principle that solvents possess distinct boiling points, which can be effectively lowered under reduced pressure conditions.

Here's a more detailed explanation of how a rotary evaporator works and its essential role in the STL process:

1. **Boiling Point Manipulation:** The key concept behind a rotary evaporator's operation is the manipulation of boiling points through vacuum and rotation. Solvents typically have boiling points at or near room temperature, making traditional evaporation methods



impractical. However, by reducing the pressure in the system, the boiling point of a solvent can be significantly lowered.

2. Rotational Motion: In the rotary evaporator, the sample is placed in a specialized flask known as the evaporation flask. This flask is attached to a rotating axis, which is precisely controlled. The rotation of the flask induces a centrifugal force that forces the sample material to spread out and form a thin film along the inner wall of the flask.

3. Vacuum System: Simultaneously, the system is subjected to a controlled vacuum environment. Lowering the pressure in the system further decreases the boiling points of the solvents, causing them to evaporate more rapidly from the thin film.

4. Condensation: The evaporated solvents, now in vapor form, are transported to a separate condenser unit. Here, they are rapidly cooled and condensed back into a liquid phase. This condensed solvent can be collected separately for disposal or further analysis.

In the Solvothermal Liquefaction (STL) process, various organic solvents such as n-hexane and heptane are often employed for their solvent properties. These solvents play a crucial role in the extraction and separation of specific components from the oil produced during the STL process.

After the STL process is complete, the oil obtained may still contain residual organic solvents. To ensure the purity and safety of the final product, these solvents must be removed. The rotary evaporator is instrumental in this separation process. It efficiently evaporates and recovers the organic solvents, leaving behind the purified oil.

The use of a rotary evaporator in the STL process enhances the efficiency and precision of solvent removal, ensuring that the final oil product is free from any residual solvents and meets the desired quality standards. This crucial step contributes to the successful and safe application of oils obtained through STL in various industrial and research applications.



*Fig (7): Rotary Evaporator.*

### 3.3 Vacuum Oven

A vacuum oven, also known as a vacuum drying oven, is a specialized piece of laboratory equipment designed to accelerate and optimize the drying process through the combined use of vacuum and heat. Its fundamental principle revolves around the manipulation of pressure to facilitate the removal of moisture, solvents, and volatile substances from various samples or materials. Here, we delve deeper into the workings and applications of vacuum ovens:

1. **Pressure Reduction:** The core concept behind a vacuum oven is the reduction of atmospheric pressure within the oven chamber. As the pressure decreases, the boiling point of liquids, including water and solvents, is significantly lowered. This reduction in boiling point enables the removal of moisture and volatile components from samples at substantially lower temperatures than would be required under standard atmospheric conditions.
2. **Uniform Heating:** Vacuum ovens are equipped with heating elements that evenly distribute heat throughout the oven chamber. This ensures consistent and controlled heating of the samples, promoting efficient drying while minimizing the risk of sample degradation.
3. **Precise Control:** Vacuum ovens come with advanced control systems that allow users to set and maintain specific temperature and pressure conditions. This level of precision is vital when working with sensitive materials or conducting experiments requiring controlled drying processes.



*Fig (8): Vacuum Oven.*

## 4. CHARACTERIZATION AND ANALYTICAL METHODS

### 4.1 GC-Mass

GC-MS, or Gas Chromatography-Mass Spectrometry, is an advanced analytical technique employed for the separation and detection of ions in the gas phase. This powerful method is utilized to determine the molecular formulas of unknown compounds, enabling precise chemical analysis.

Here's an expanded explanation of how GC-MS works:

1. **Sample Introduction:** The process begins with the introduction of the sample into the vacuum system of the mass spectrometer through an inlet.
2. **Ionization:** Within the source region of the mass spectrometer, neutral sample molecules undergo ionization, where they are transformed into ions. These ions are then accelerated into the mass analyzer.
3. **Mass Analyzer:** The mass analyzer serves as the core component of the mass spectrometer. It plays a pivotal role in separating ions based on their mass-to-charge ratio ( $m/z$ ). This separation can occur either in space or over time, depending on the specific type of mass analyzer used.
4. **Ion Detection:** Once the ions are successfully separated, they are detected by a specialized detector. The resulting signals are then transmitted to a data system for further analysis and processing.

5. Vacuum System: All mass spectrometers are equipped with a vacuum system to maintain a low-pressure environment, often referred to as high vacuum. This high vacuum condition is crucial for optimal instrument performance. It serves to minimize undesired effects such as ion-molecule reactions, scattering, and ion neutralization, which can distort the accuracy of the analysis.

In this study, the objective was to analyze the components present in crude oil derived from waste plastics. The following method was employed: GC/MS Analysis: Crude oil samples were subjected to GC/MS analysis using a modified Petroleum Refinery Reformate standard procedure (Corporation, 2010). The analysis was conducted using an Agilent 7890 A GC instrument equipped with a ZB-5 ms column ( $30\text{ m} \times 0.25\text{ mm I.D.} \times 0.25\text{ }\mu\text{m}$  film thickness). Injections of  $1\text{ }\mu\text{L}$  were made in a spitless mode. The oven program commenced at  $40\text{ }^{\circ}\text{C}$  and was held for 4 minutes before ramping up at  $5\text{ }^{\circ}\text{C/min}$  to  $110\text{ }^{\circ}\text{C}$ . Subsequently, it was further ramped to  $320\text{ }^{\circ}\text{C}$  at a rate of  $3\text{ }^{\circ}\text{C/min}$ . This methodology allowed for the precise separation and identification of the components present in the crude oil, providing valuable insights into its chemical composition and properties.

#### 4.2 TGA

Thermogravimetric Analysis (TGA) is a technique in thermal analysis that provides valuable insights into various physical and chemical phenomena as a sample undergoes controlled temperature changes over time. This method is instrumental in investigating phase transitions, absorption and desorption processes, as well as chemical phenomena like chemisorption, thermal decomposition, and solid-gas reactions.

Here's a detailed explanation of how TGA works:

1. **Sample Heating:** A sample is placed in a controlled environment, which can be air, nitrogen (N<sub>2</sub>), carbon dioxide (CO<sub>2</sub>), helium (He), argon (Ar), or other gases, depending on the specific analysis requirements. The sample is then heated at a constant rate.
2. **Measurement of Mass Change:** As the temperature of the sample increases, various physical and chemical transformations take place. One of the key parameters monitored during TGA is the change in the sample's mass. This mass change is recorded as a function of temperature or time throughout the experiment.
3. **Data Collection:** The TGA instrument continuously records the sample's weight as it evolves during heating. This data is essential for constructing thermogravimetric curves, also known as thermograms.

The plot of weight change (mass loss or gain) against temperature or time is referred to as a thermogravimetric curve or thermogram. These curves reveal critical information about the sample's behavior under varying temperature conditions.

In this specific study, TGA was employed to calculate the proximate analysis parameters, including volatile matter (VM), ash content (AC), and fixed carbon (FC), for the feedstock, char, and crude oil. The analysis involved heating approximately 10 mg of the dry sample from room temperature to 925°C at a constant heating rate of 20°C/min. This process was conducted under a nitrogen flow rate of 50 ml/min and a purge flow rate of 30 ml/min using a NETZSCH TG 209 Libra thermal analyzer from Germany.

To provide a comprehensive analysis and interpretation of the results, it would be helpful to include the actual TGA curve or an image depicting the weight change of the sample as a function of temperature. This visual representation would offer a clear illustration of the sample's behavior during the TGA analysis and facilitate a more in-depth understanding of the proximate analysis and thermal characteristics of the materials studied.

#### 4.3 Bomb Calorimeter

A bomb calorimeter is a critical instrument used to measure the changes in a system's internal energy resulting from a chemical reaction. It operates on the fundamental principle that a chemical reaction releases heat, and this heat can be precisely quantified. Here's an in-depth explanation of how a bomb calorimeter functions and its role in your research:

1. **Sealed Reaction Container:** The heart of a bomb calorimeter is a sealed container known as a bomb. Inside this bomb, a carefully measured quantity of the sample or feedstock (in this case, solid residue or oil generated from plastic) is placed. This bomb is designed to withstand the high pressure generated during the combustion reaction.
2. **Insulated Container:** The bomb is placed in an insulated container that prevents heat exchange with the surroundings. This ensures that the heat generated by the combustion reaction remains within the system and is not lost to the environment.
3. **Stirring and Temperature Monitoring:** The calorimeter setup includes a stirrer to ensure uniform mixing of the reaction products. A thermometer is also present to monitor the temperature changes accurately.



4. Electric Ignition: The combustion reaction is initiated through an electric ignition system. When the reaction is triggered, the sample inside the bomb combusts in the presence of oxygen.

5. Heat Transfer: As the sample undergoes combustion, it releases heat energy. This energy raises the temperature of the surrounding water, which acts as a heat sink. It is crucial to maintain a constant temperature throughout the surrounding water, which is achieved with the help of the thermometer.

6. Calorimetry: By carefully measuring the temperature change of the surrounding water and knowing its heat capacity, it is possible to calculate the heat released during the combustion reaction. This heat value is the calorific value of the sample and is typically expressed in units such as joules per gram (J/g) or megajoules per kilogram (MJ/kg).

In this research, a bomb calorimeter, specifically the Parr Model 6725 Semi-micro calorimeter from Moline, IL, was employed to estimate the Higher Heating Value (HHV) of the materials in megajoules per kilogram (MJ/kg). This measurement is crucial for understanding the energy content of the products derived from the combustion of feedstock, solid residue, or plastic-generated oil. Additionally, the elemental composition of the products was determined using a CHNS/O elemental analyzer, providing valuable insights into their chemical composition.

To ensure the accuracy of these analyses, ultra-high-purity gases (nitrogen and oxygen) were used during the operation of the TGA (Thermogravimetric Analysis), the bomb calorimeter, and the CHNS/O elemental analyzer. This rigorous approach ensures the reliability and precision of the data obtained in this research.

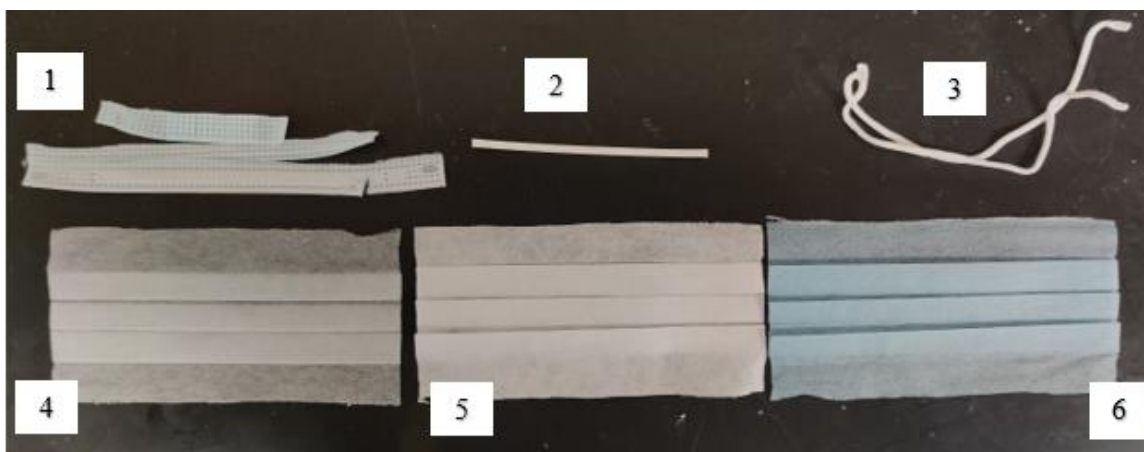


*Fig (9): Oxygen Bomb Calorimeter.*

## 5. MATERIALS AND METHODS

### 5.1 Materials

The feedstock used in this experiment is the 3-layered facemask from KmK[47]. The fabric used for the face masks is non-woven fabric. From the fig below 1. Ultrasonic welded edge pieces, 2. Nose wire, 3. Elasticated ear-loop, 4. Outer layer, 5. Filter layer, 6. Inner layer [48]. Except 2 and 3 very thing is made of PP.

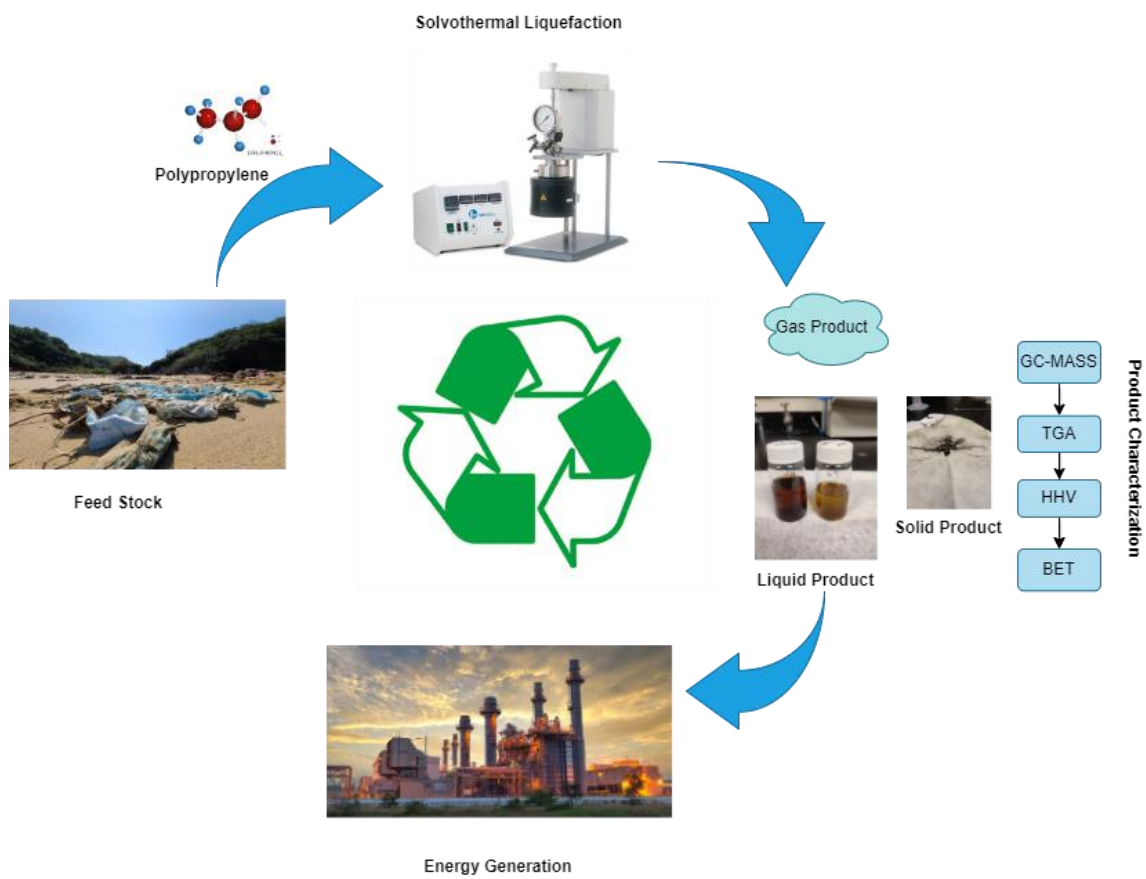


*Fig (10): Sections of 3-layered Face Masks.*

### 5.2 Methods

The solvo-thermal liquefaction experiments were performed in a stainless-steel reactor (Model 4593, Parr Instrument Company, Moline, IL). The setup contains a reactor with an inner volume of 100 ml, a mechanical stirrer, and an electric heater controlled by a 4843 controller. In a typical experimental run, 2 gm of PP plastic and 14 ml of solvent were added to the reactor. The reactor is then sealed and purged with high-purity nitrogen to create an inert environment for the reactants. After the purging process, the initial before the reaction started pressure of 200 psi was maintained in the reactor. The temperature is increased at a rate of 6 degrees per minute till it reached the desired temperature, after the

desired temperature is reached the reaction residence time begins. The reactor was cooled down to room temperature after the reaction finished and an electric fan was used to speed up the process, then the incondensable gases were collected by a gasbag, and the reactor was then opened. The average time is around 2 hr for heating and cooling the reactor. In the STL systems, the products are filtered directly without extraction and phase separation. The contents (liquid and solid mixture) were then transferred to a glass separating funnel equipped with a dried and preweighed filter paper (Whatman filter paper #4) to separate the solid from the liquid fraction. The solid fraction was dried in an oven at 60 °C for > 6 h and termed as a solid residue. All the crude oil and liquid fractions were stored (under ~5 °C) for further analysis. A series of experiments were carried out to investigate the effect of temperature in the reaction, and the effect of residence time in the reaction: (1) STL reactions were carried out using two different solvents n-hexene and heptane ; (2) Hex STL reactions were carried out under the different residence times ranging from 30 - 90 mins at 350 °C with 1:7solid liquid ratio;(3) STL under the different temperature conditions like 300,325,350 °C were carried out for 30 mins with 1:7solid-liquid ratio.



*Fig (11): Schematic View of the Whole Process.*

## 6. RESULTS AND DISCUSSION

### 6.1 Effect of Solvent Type

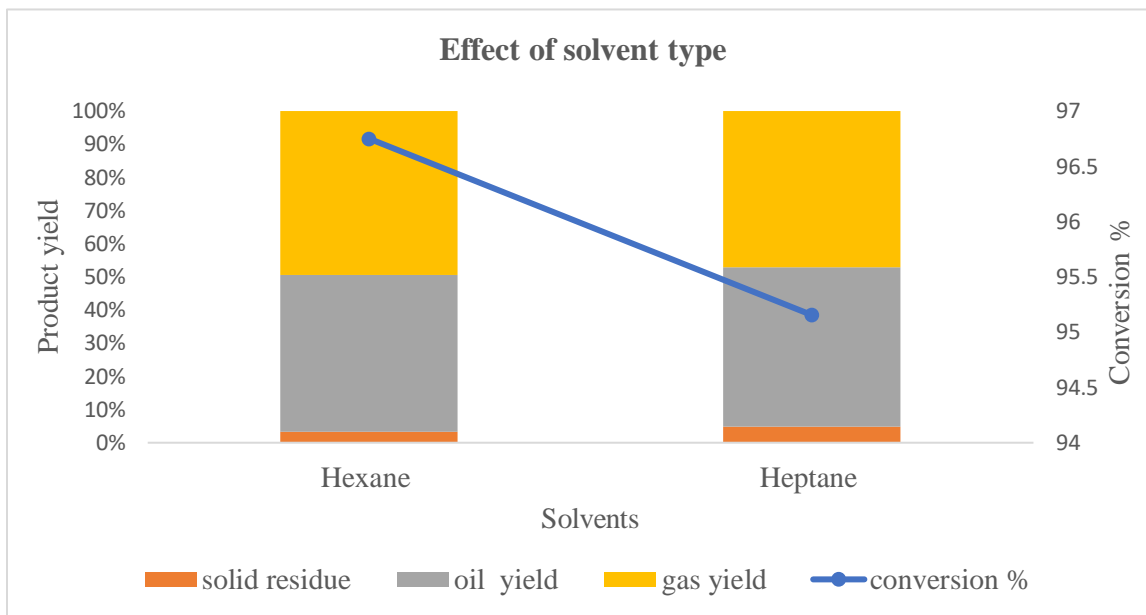
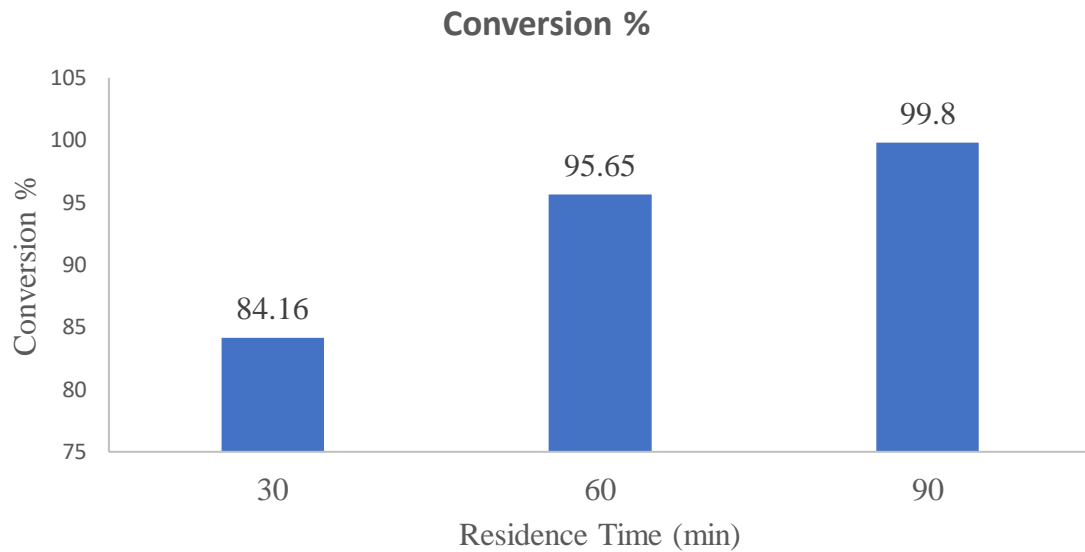


Fig (12): Variations of Product Fraction Yields from PP-facemasks Using Different Solvents.

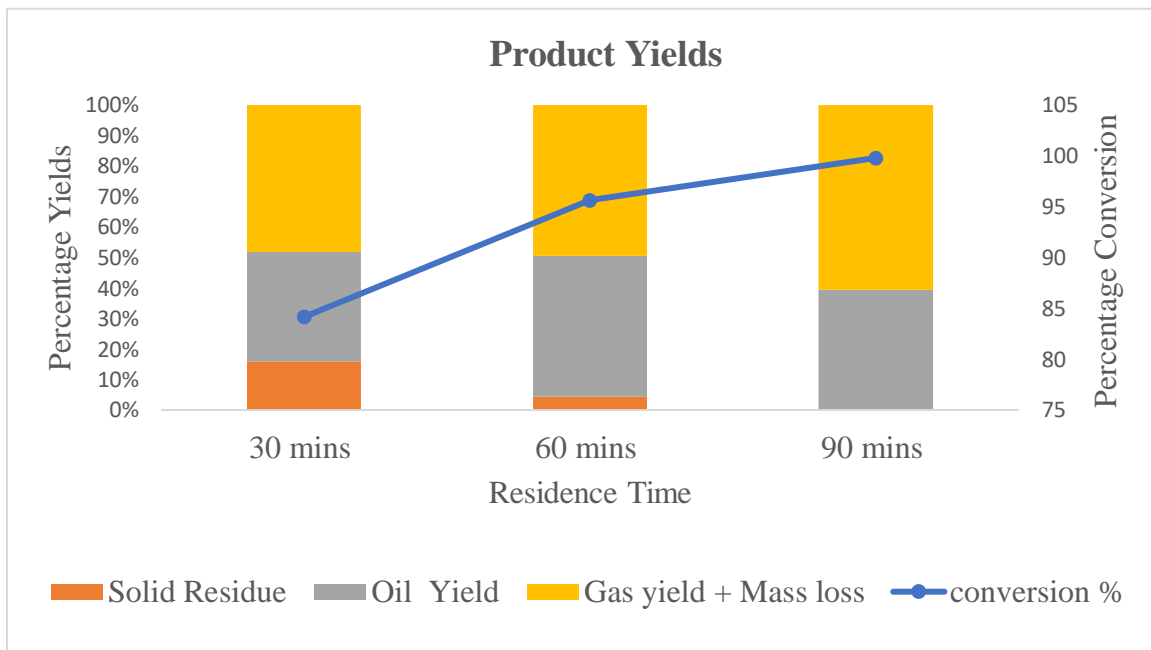
The depolymerization of PP-face masks was carried out using STL. To understand the effects of different solvents on the PP-face mask depolymerization, experiments were carried out with two types of organic solvents hexane and heptane under different conditions ranging from 30 – 90 mins residence time, 300 – 350 °C reaction temperature, and the feed intel ratios of 1:7 solid to liquid ratio. The hexane treatment has achieved the highest conversion rate of 96.75% at 350 °C at 90 min, and its products contain 47.25% oil yield, 3.45% solid residue and 49.53 % gas plus losses. Compared with heptane 95.15% conversion which is a bit lesser than hexane. However, the oil yield was more from heptane 48.12% compared to hexane. Additionally, the gas yield plus losses were less for heptane

by around 47.04%. Whereas 96% of crude oil is obtained from PP by Hwang et al [28] through conditions around 450-470 °C and 30 mins in acetone solvent. However, due to the higher reaction temperature and the energy used to extract acetone from the liquid layer. PP-STL with acetone is not economically viable for industries due to its high energy input for higher reaction temperatures and extraction of acetone. Therefore, organic solvents like n-hexane and heptane are very useful for STL-PP because they have high conversion rates at lower reaction temperatures (350 °C) and exclude the extraction step which is usually done while using a solvent. Additionally, hexane and heptane will also help in improving the HHV of the crude oil. According to Yanmin Wang[27] and Pinero-Hernanz [49] et al., the thermal degradation polymer mainly depends on the solvation capability of the solvent with respect to the polymer. The solvation capability mainly depends on the dipole moments and the dielectric constant of the solvent. Moreover, the dielectric constant of solvent molecules varies with temperature. In sup/subcritical state, the dielectric constant of the solvent decreases compared with that at room temperature, which makes the solvent have stronger solvation capability. The supercritical temperatures of n-hexane and heptane are similar compared to traditional solvents like acetone. Polypropylene (PP) is a semi-crystalline, non-polar thermoplastic polymer that melts at 160 °C. when depolymerization of PP is carried out at 350 °C, organic solvents (n-hexane heptane) at supercritical conditions disperse and dissolve PP. Therefore, the solvolysis process with organic solvents can decompose PP more effectively and generate higher oil and gas yields economically.

## 6.2 Effect of Residence Time



*Fig (13): Conversion Percentages Using Different Residence Time.*



*Fig (14): Variations of Product Fraction Yields from PP-facemasks Using Different Residence times (30, 60, 90) Min.*



In PP-Face mask depolymerization using solvothermal liquefaction, residence time plays an important role. The experiments were conducted at different times ranging from 30 – 90 min using hexane as the solvent and keeping the temperature and the pressure constant at 350 °C and 200 psi respectively. The rate of conversion was highest at 90 mins at 99.8 %. From the above *Fig (13)*, it is very clear that the percentage conversion has decreased as the residence time decreased at 30 mins residence time the percentage conversion was at 84.16 % and for the 60 mins residence time conversion was at 95.65 %.

From *Fig (14)* we can understand more about the effects caused by the changes in the residence time on the product fraction yields. As the residence time increases from 30 – 90 min, The solid residue decreases from 15.83% - 0.2 %, The oil yield increases from 35.93% - 39.3%, and the gas yield also increases from 48.22 – 60.5 %.

A key observation from *Fig (14)* is that the oil yield reaches its peak at 60 minutes, with a notable percentage of 46.35%. However, when the experiment is extended to 90 minutes at a higher temperature, the oil yield drops to 39.3%. This indicates that for a given temperature, as the residence time increases, the oil yield also increases for a certain point, while the percentage of solid residue conversion decreases, leading to an enhanced conversion rate. Several factors contribute to this phenomenon, including the complete breakdown of PP material, improved heat transfer over longer residence times, and a reduction in the formation of unwanted byproducts.

This trend in the impact of residence time on the reaction processes and product yield aligns with findings from other liquefaction reactions involving polymers [22] [48].

### 6.3 Effect of Change in Temperature:

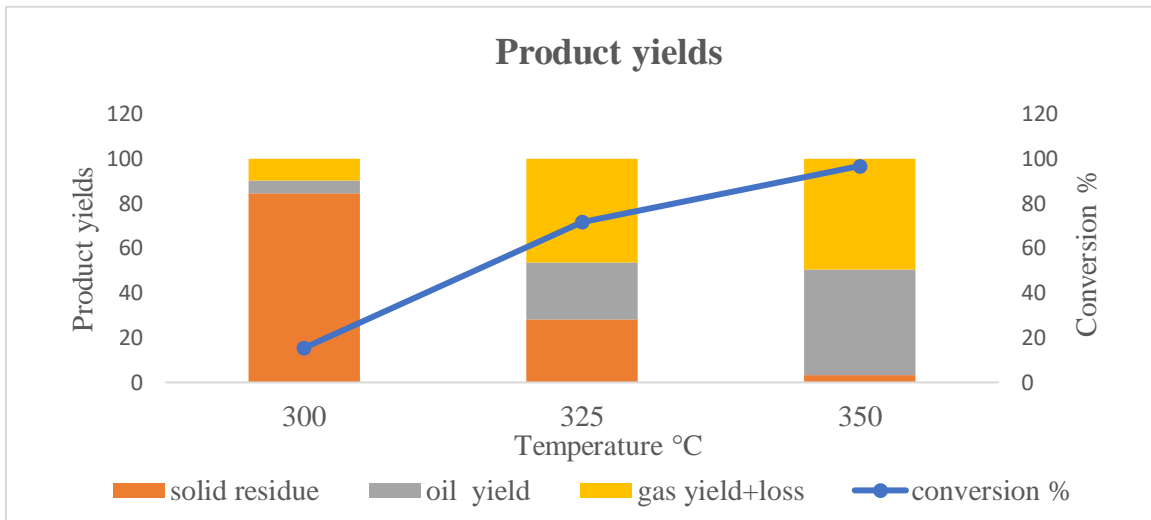


Fig (15): Variations of Product Fraction Yields from PP-facemasks Using Different Temperatures (300, 325, 350 °C).

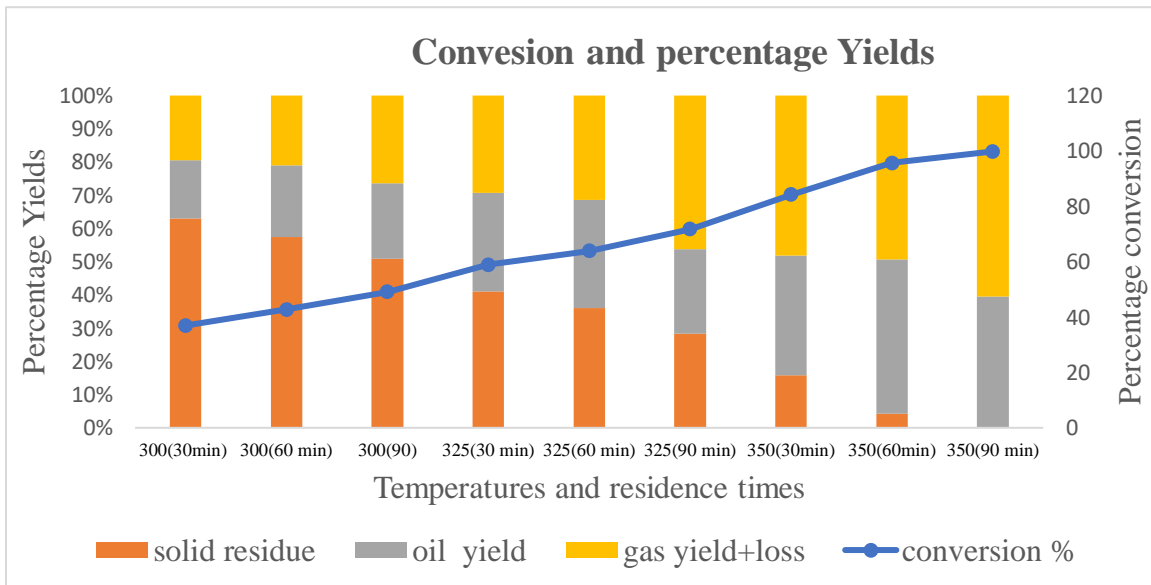
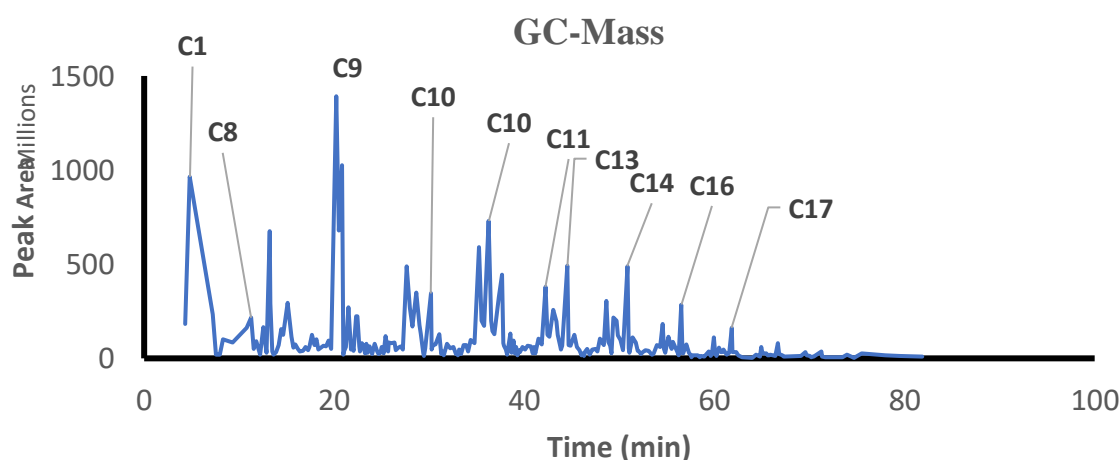


Fig (16): Variations of Product fraction Yields from PP-facemasks Using Different Temperatures (300,325,350 °C) and Different Residence times (30,60,90 Min).

Temperature plays an important role in thermal liquefaction. The experiments were conducted at different temperatures ranging from 300 – 350 °C at constant residence time

(90 min), using hexane as the solvent. The lowest conversion rate was 49.04 % at 300 °C and the highest conversion rate was around 99.8 % at 350 °C. Similarly, the oil and gas yields kept increasing with increasing temperature. The effect of reaction temperature on the reaction processes and the product yield is similar to that of the other polymer liquefaction reactions [22], [50].

#### 6.4 GC-Mass Analysis Of The Oil Product



*Fig (17): GC-Mass Data of the Crude Oil Using Hexane solvent.*

During the process of solvothermal liquefaction of PP face masks, one of the primary products obtained is crude oil. To gain a more comprehensive understanding of the mechanisms involved in the PP thermal liquefaction reactions, the chemical composition of the crude oil [350 °C, 90 min] is analyzed using Gas Chromatography-Mass Spectrometry (GCMS). The components identified through this analysis can be categorized into four main groups, as outlined in Table 5. The predominant constituents within the crude oil resulting from PP thermal liquefaction are alkanes and alkenes, with a notable presence of compounds falling within the C8 to C17 range. Table 5 provides a detailed list

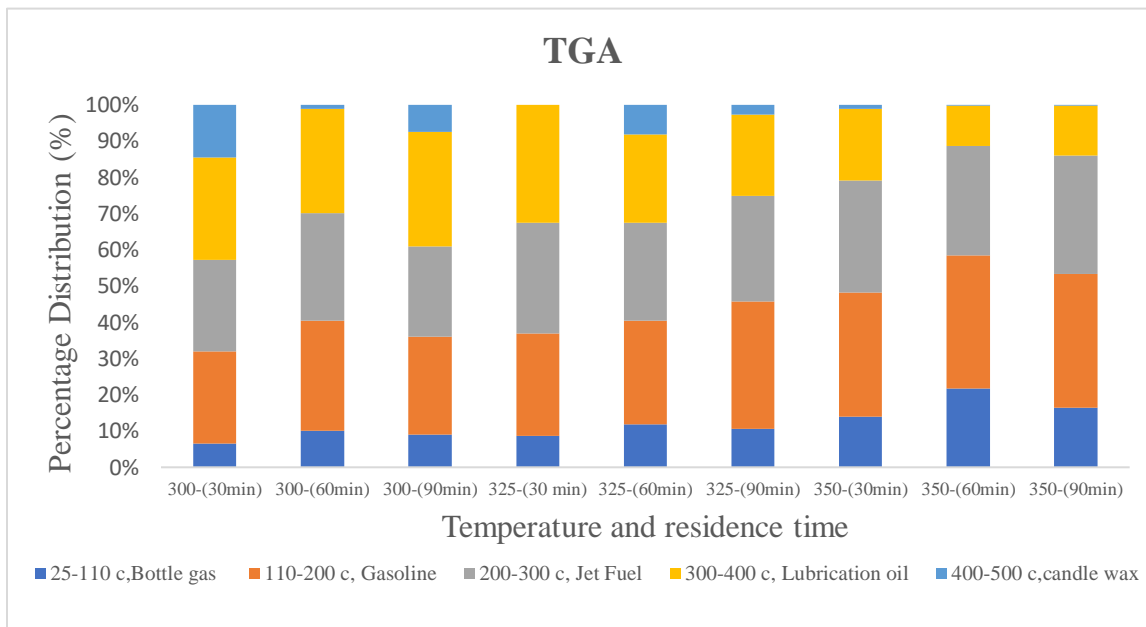
of the different alkanes, alkenes, cyclanes, and heteroatomic hydrocarbons identified in the crude oil.

*Table (5): Classification of Crude Oil Composition.*

<b>Alkanes</b>	<b>Chemical formula</b>
hexane2,3,4, -trimethyl	C <sub>9</sub> H <sub>20</sub>
decane	C <sub>10</sub> H <sub>22</sub>
octane,2,4,6-trimethyl	C <sub>11</sub> H <sub>24</sub>
2-dodecane,4-methyl	C <sub>13</sub> H <sub>28</sub>
hexadecane	C <sub>16</sub> H <sub>34</sub>
<b>Alkenes</b>	
1-heptene,5-methyl	C <sub>8</sub> H <sub>16</sub>
1-octene,3,3-dimethyl	C <sub>10</sub> H <sub>20</sub>
<b>Cyclanes</b>	
cyclohexane, undecyl	C <sub>17</sub> H <sub>34</sub>
cyclohexane octyl	C <sub>14</sub> H <sub>28</sub>
cyclohexane,3,3,5-trimethyl	C <sub>9</sub> H <sub>16</sub>
<b>Heteroatomic hydrocarbons</b>	
1-pentyn-1-ol,4-methyl	C <sub>6</sub> H <sub>10</sub> O
1-heptanol,4methyl	C <sub>8</sub> H <sub>16</sub> O
2-tetradecanol	C <sub>14</sub> H <sub>30</sub> O

Furthermore, Figure (17) illustrates a plot depicting the relationship between peak area and time, showcasing the presence of various components at distinct time intervals. This data contributes to a more in-depth understanding of the composition and evolution of the crude oil generated during the PP thermal liquefaction process.

## 6.5 TGA Of The Oil Product



*Fig (18): TGA Data of the Crude Oil Using Hexane Solvent at Different Temperatures and Pressures.*

The TGA analysis, which encompassed a range of temperatures (300°C to 350°C) and different residence times (30 minutes to 90 minutes), provided valuable insights into the composition and characteristics of the products obtained from the depolymerization of PP plastic light. Here are additional points to consider regarding the findings from this analysis:

1. Effect of Temperature and Residence Time: The observed trend in Fig (18) clearly illustrates the influence of temperature and residence time on the composition of the oil produced. As you moved from lower temperatures and shorter residence times towards higher values, several key changes became evident.

2. Shift in Composition: As temperature and residence time increased, there was a noticeable shift in the composition of the products. This shift was characterized by an increase in bottle gas percentage and a decrease in candle wax percentage. This trend suggests that the higher temperature and longer residence times favored the production of lighter hydrocarbon fractions, such as gases and lighter liquid fuels.

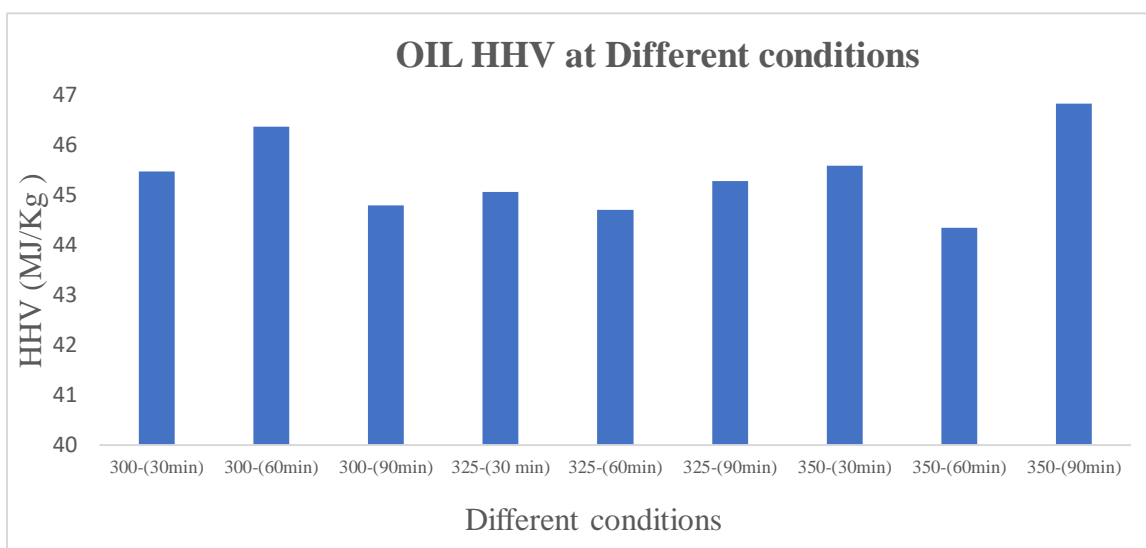
3. Lubrication Oil and Candle Wax: At the conditions of 330°C for 30 minutes, the samples exhibited higher percentages of candle wax (28.366%) and lubrication oil (14.438%). This finding implies that under these specific conditions, the depolymerization process produced heavier and more viscous oils, which may have limited utility compared to lighter fuels.

4. Jet Fuel and Gasoline: The most significant percentages of jet fuel (32.581%) and gasoline (36.0909%) were obtained at the highest temperature and longest residence time, specifically at 350°C for 90 minutes. This indicates that these conditions were optimal for the depolymerization of PP plastic lighters to yield valuable lighter hydrocarbon products.

5. Optimization of Conditions: These results suggest the importance of carefully optimizing the depolymerization conditions to target specific products. Depending on the desired end products (e.g., lighter fuels or heavier oils), adjusting the temperature and residence time can have a significant impact on the composition and properties of the oil produced.

6. Economic and Environmental Considerations: The findings also have implications for the economic and environmental aspects of the process. Optimizing conditions to favor the production of lighter, more valuable fuels can enhance the economic viability of the depolymerization process while potentially reducing the environmental impact associated with the disposal of plastic waste.

## 6.6 HHV Of The Oil Product



*Fig (19): HHV Data of the Crude Oil Using Hexane Solvent at Different Temperatures and Pressures.*

The HHV (Higher Heating Value) experiments provided valuable insights into the energy content of the oil product obtained from the STL (Solvent Thermal Liquefaction) experiments. Here are some key points to highlight based on the findings from Fig (19):

1. High Heating Value: The results indicate that all samples obtained at different temperatures and residence times exhibited high HHV values, approximately close to 45 MJ/kg. This observation is significant because it suggests that the oil products derived from the STL process possess a substantial energy content.
2. Comparison with Commercial Fuels: It's noteworthy that the HHV values obtained for oil products are notably higher than the HHV of some commercially available fuels, such as gasoline (HHV  $\approx$  43.4 MJ/kg). This finding underscores the potential energy value of the oil produced from PP plastic through your STL process.
3. Optimal Conditions: The highest HHV was achieved at 350°C for 90 minutes, with a value of 46.816 MJ/kg. This finding highlights the importance of optimizing the reaction conditions to maximize the energy content of the oil product. These conditions appear to be particularly effective in enhancing the energy value of the oil.
4. Hexane vs. Oil: It's interesting to note that the high HHV values observed in the oil products are not solely attributed to the solvent hexane. Hexane itself has an HHV of approximately 44.752 MJ/kg. Therefore, the significant increase in HHV is primarily due to the composition of the oil generated from the PP plastic.
5. Energy Potential: The results suggest that the oil obtained from PP plastic has a remarkable energy potential, making it a valuable resource for energy generation and possibly as an alternative or supplementary fuel source.



In conclusion, HHV experiments demonstrated that the oil produced from the STL process has a significantly high energy content, surpassing that of some commercially available fuels. This finding underscores the potential in both energy production and waste management, with broader implications for sustainability and environmental conservation.

## CONCLUSION

This study delves into the exploration of PP's thermal liquefaction reaction using hexane and heptane as the solvents. Our investigation involved a comprehensive examination of various reaction conditions, encompassing reaction conversion (%), oil yields, calorific value, energy recovery rate, and the presence of low molecular weight components in the resulting oil.

The findings illuminate the value of hexane-based solvothermal liquefaction (STL) of PP, particularly as a valuable source of fuel gas. Consequently, further in-depth analysis on the gas phase of this process holds substantial research significance. Furthermore, the use of organic solvents in gasifying waste plastics demonstrates considerable potential for research and development in the field.

Incorporating thermogravimetric analysis into our study, we effectively simulated the crude distillation process. This approach enabled us to acquire crucial guidance regarding industrial valorization, particularly with regard to the boiling range of components. Notably, PP liquefied oil showcases a high concentration of low-boiling-point hydrocarbon chains, a consequence of the relatively moderate reaction conditions. Additionally, the oil exhibits a low content of aromatic components, minimal complex cyclization aromatization reactions, and negligible levels of nitrogen and oxygen. These properties render the physical and chemical attributes of PP liquefied oil superior to those of petroleum crude oil. As such, it emerges as a promising high-quality substitute for petroleum crude oil and a potential source of platform compounds.

This study underscores the compatibility of existing crude oil processing equipment with the refining of PP liquefied oil. Moreover, the solvation of the sample within the thermal liquefaction system substantially reduces the thermal degradation temperature of PP. Within the context of solvothermal liquefaction, thermal cracking predominantly influences the two reactions, with solvolysis playing a minor role. The random scission pathway emerges as the dominant process in feedstock degradation. Given the decisive role of solvation in solvent thermal liquefaction reactions, our research emphasizes the significance of polarity analysis for sample-solvent matching.

Looking ahead, the establishment of a solvent dipole moment database and the model fitting and experimental verification of the dielectric constant, in conjunction with parameters like temperature, hold great potential. These efforts will guide solvent and temperature selection, thereby driving advancements in thermal liquefaction technology.

In conclusion, our exploration of PP thermal liquefaction with hexane as a solvent reveals promising avenues for sustainable fuel production and waste plastic valorization. This research not only enhances our understanding of the process but also lays the foundation for further advancements in solvent-based plastic waste conversion technologies.

## REFERENCES

- [1] P. De, I. Chakraborty, B. Karna, and N. Mazumder, “Brief review on repurposed drugs and vaccines for possible treatment of COVID-19,” *European Journal of Pharmacology*, vol. 898. Elsevier B.V., May 05, 2021. doi: 10.1016/j.ejphar.2021.173977.
- [2] İ. Aygün, M. Kaya, and R. Alhajj, “Identifying side effects of commonly used drugs in the treatment of Covid 19,” *Sci Rep*, vol. 10, no. 1, Dec. 2020, doi: 10.1038/s41598-020-78697-1.
- [3] S. Feng, C. Shen, N. Xia, W. Song, M. Fan, and B. J. Cowling, “Rational use of face masks in the COVID-19 pandemic,” *The Lancet Respiratory Medicine*, vol. 8, no. 5. Lancet Publishing Group, pp. 434–436, May 01, 2020. doi: 10.1016/S2213-2600(20)30134-X.
- [4] J. Howard *et al.*, “An evidence review of face masks against COVID-19,” *Proceedings of the National Academy of Sciences of the United States of America*, vol. 118, no. 4. National Academy of Sciences, Jan. 26, 2021. doi: 10.1073/pnas.2014564118.
- [5] C. Crespo, G. Ibarz, C. Sáenz, P. Gonzalez, and S. Roche, “Study of Recycling Potential of FFP2 Face Masks and Characterization of the Plastic Mix-Material Obtained. A Way of Reducing Waste in Times of Covid-19,” *Waste Biomass Valorization*, vol. 12, no. 12, pp. 6423–6432, Dec. 2021, doi: 10.1007/s12649-021-01476-0.
- [6] T. A. Aragaw, “Surgical face masks as a potential source for microplastic pollution in the COVID-19 scenario,” *Mar Pollut Bull*, vol. 159, Oct. 2020, doi: 10.1016/j.marpolbul.2020.111517.
- [7] T. Atugoda *et al.*, “Interactions between microplastics, pharmaceuticals and personal care products: Implications for vector transport,” *Environment International*, vol. 149. Elsevier Ltd, Apr. 01, 2021. doi: 10.1016/j.envint.2020.106367.
- [8] J. 26, 2022 Wenyi Zhang, “Annual production volume of face masks in China 2017-2021.”
- [9] W. Niu *et al.*, “Polypropylene: now available without chain ends,” *Chem*, vol. 5, no. 1, pp. 237–244, 2019.
- [10] R. R. Bora, R. Wang, and F. You, “Waste polypropylene plastic recycling toward climate change mitigation and circular economy: energy, environmental, and

- technoeconomic perspectives,” *ACS Sustain Chem Eng*, vol. 8, no. 43, pp. 16350–16363, 2020.
- [11] X. Chen, Y. Wang, and L. Zhang, “Recent Progress in the Chemical Upcycling of Plastic Wastes,” *ChemSusChem*, vol. 14, no. 19. John Wiley and Sons Inc, pp. 4137–4151, Oct. 05, 2021. doi: 10.1002/cssc.202100868.
  - [12] W. d’Ambrières, “Plastics recycling worldwide: current overview and desirable changes,” *Field Actions Science Reports. The journal of field actions*, no. Special Issue 19, pp. 12–21, 2019.
  - [13] “Plastics: Material-Specific Data.”
  - [14] M. Potrykus *et al.*, “Polypropylene structure alterations after 5 years of natural degradation in a waste landfill,” *Science of the Total Environment*, vol. 758, Mar. 2021, doi: 10.1016/j.scitotenv.2020.143649.
  - [15] D. Pan, F. Su, C. Liu, and Z. Guo, “Research progress for plastic waste management and manufacture of value-added products,” *Adv Compos Hybrid Mater*, vol. 3, no. 4, pp. 443–461, 2020.
  - [16] G. K. Parku, F.-X. Collard, and J. F. Görgens, “Pyrolysis of waste polypropylene plastics for energy recovery: Influence of heating rate and vacuum conditions on composition of fuel product,” *Fuel Processing Technology*, vol. 209, p. 106522, 2020.
  - [17] P. T. Williams and E. Slaney, “Analysis of products from the pyrolysis and liquefaction of single plastics and waste plastic mixtures,” *Resour Conserv Recycl*, vol. 51, no. 4, pp. 754–769, 2007.
  - [18] A. Buekens, “Introduction to feedstock recycling of plastics,” *Feedstock recycling and pyrolysis of waste plastics*, vol. 6, no. 7, pp. 1–41, 2006.
  - [19] M. Goto, “Supercritical water process for the chemical recycling of waste plastics,” in *AIP conference proceedings*, American Institute of Physics, 2010, pp. 169–172.
  - [20] T. Nakagawa and M. Goto, “Recycling thermosetting polyester resin into functional polymer using subcritical water,” *Polym Degrad Stab*, vol. 115, pp. 16–23, 2015.
  - [21] M. Goto, M. Sasaki, and T. Hirose, “Reactions of polymers in supercritical fluids for chemical recycling of waste plastics,” *J Mater Sci*, vol. 41, no. 5, pp. 1509–1515, 2006.

- [22] M. S. Seshasayee and P. E. Savage, "Oil from plastic via hydrothermal liquefaction: Production and characterization," *Appl Energy*, vol. 278, p. 115673, 2020.
- [23] S. Raikova, T. D. J. Knowles, M. J. Allen, and C. J. Chuck, "Co-liquefaction of macroalgae with common marine plastic pollutants," *ACS Sustain Chem Eng*, vol. 7, no. 7, pp. 6769–6781, 2019.
- [24] I. Okajima, K. Watanabe, and T. Sako, "Chemical recycling of carbon fiber reinforced plastic with supercritical alcohol," *J Adv Res Phys*, vol. 3, no. 2, pp. 1–4, 2012.
- [25] I. Okajima, M. Hiramatsu, Y. Shimamura, T. Awaya, and T. Sako, "Chemical recycling of carbon fiber reinforced plastic using supercritical methanol," *J Supercrit Fluids*, vol. 91, pp. 68–76, 2014.
- [26] P. Zhao, Z. Yuan, X. Song, J. Zhang, and A. J. Ragauskas, "Product characteristics and synergy study on supercritical methanol liquefaction of lignocellulosic biomass and plastic," *ACS Sustain Chem Eng*, vol. 9, no. 50, pp. 17103–17111, 2021.
- [27] Y. Wang and F.-S. Zhang, "Degradation of brominated flame retardant in computer housing plastic by supercritical fluids," *J Hazard Mater*, vol. 205, pp. 156–163, 2012.
- [28] G. C. Hwang, K. H. Kim, S. Y. Bae, S. C. Yi, and H. Kumazawa, "Degradation of high density polyethylene, polypropylene and their mixtures in supercritical acetone," *Korean Journal of Chemical Engineering*, vol. 18, no. 3, pp. 396–401, 2001.
- [29] Y. Liu *et al.*, "Effective depolymerization of polyethylene plastic wastes under hydrothermal and solvothermal liquefaction conditions," *Chemical Engineering Journal*, vol. 446, p. 137238, 2022, doi: <https://doi.org/10.1016/j.cej.2022.137238>.
- [30] "Heptane and hexane in gasoline ," <https://ecolink.com/info/heptane-and-hexane-in-gasoline/>.
- [31] R. Miandad, M. A. Barakat, A. S. Aburizaiza, M. Rehan, and A. S. Nizami, "Catalytic pyrolysis of plastic waste: A review," *Process Safety and Environmental Protection*, vol. 102, pp. 822–838, 2016, doi: <https://doi.org/10.1016/j.psep.2016.06.022>.
- [32] X. Yang, L. Sun, J. Xiang, S. Hu, and S. Su, "Pyrolysis and dehalogenation of plastics from waste electrical and electronic equipment (WEEE): A review," *Waste*

*Management*, vol. 33, no. 2, pp. 462–473, 2013, doi:  
<https://doi.org/10.1016/j.wasman.2012.07.025>.

- [33] Y. Liu *et al.*, “Effective depolymerization of polyethylene plastic wastes under hydrothermal and solvothermal liquefaction conditions,” *Chemical Engineering Journal*, vol. 446, Oct. 2022, doi: 10.1016/j.cej.2022.137238.
- [34] J. Liu, Z. Jiang, H. Yu, and T. Tang, “Catalytic pyrolysis of polypropylene to synthesize carbon nanotubes and hydrogen through a two-stage process,” *Polym Degrad Stab*, vol. 96, no. 10, pp. 1711–1719, 2011.
- [35] J. Gong *et al.*, “Sustainable Conversion of Mixed Plastics into Porous Carbon Nanosheets with High Performances in Uptake of Carbon Dioxide and Storage of Hydrogen,” *ACS Sustain Chem Eng*, vol. 2, no. 12, pp. 2837–2844, Dec. 2014, doi: 10.1021/sc500603h.
- [36] Y. Chai, N. Gao, M. Wang, and C. Wu, “H<sub>2</sub> production from co-pyrolysis/gasification of waste plastics and biomass under novel catalyst Ni-CaO-C,” *Chemical Engineering Journal*, vol. 382, p. 122947, 2020.
- [37] G. Lopez, M. Artetxe, M. Amutio, J. Alvarez, J. Bilbao, and M. Olazar, “Recent advances in the gasification of waste plastics. A critical overview,” *Renewable and Sustainable Energy Reviews*, vol. 82, pp. 576–596, 2018, doi: <https://doi.org/10.1016/j.rser.2017.09.032>.
- [38] A. Arregi *et al.*, “CeO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub> Promoters in the Steam Reforming of Polyolefinic Waste Plastic Pyrolysis Volatiles on Ni-Based Catalysts,” *ACS Sustain Chem Eng*, vol. 8, no. 46, pp. 17307–17321, Nov. 2020, doi: 10.1021/acssuschemeng.0c06800.
- [39] Y. Park, T. Namioka, S. Sakamoto, T. Min, S. Roh, and K. Yoshikawa, “Optimum operating conditions for a two-stage gasification process fueled by polypropylene by means of continuous reactor over ruthenium catalyst,” *Fuel Processing Technology*, vol. 91, no. 8, pp. 951–957, 2010, doi: <https://doi.org/10.1016/j.fuproc.2009.10.014>.
- [40] S. S. Toor *et al.*, “Hydrothermal liquefaction of *Spirulina* and *Nannochloropsis salina* under subcritical and supercritical water conditions,” *Bioresour Technol*, vol. 131, pp. 413–419, 2013.
- [41] R. X. Yang, K. Jan, C. T. Chen, W. T. Chen, and K. C. W. Wu, “Thermochemical Conversion of Plastic Waste into Fuels, Chemicals, and Value-Added Materials: A Critical Review and Outlooks,” *ChemSusChem*, vol. 15, no. 11. John Wiley and Sons Inc, Jun. 08, 2022. doi: 10.1002/cssc.202200171.

- [42] N. Ghavami, K. Özdenkçi, G. Salierno, M. Björklund-Sänkiahö, and C. De Blasio, “Analysis of operational issues in hydrothermal liquefaction and supercritical water gasification processes: a review,” *Biomass Conversion and Biorefinery*. Springer Science and Business Media Deutschland GmbH, Sep. 01, 2021. doi: 10.1007/s13399-021-02176-4.
- [43] K. Jin, P. Vozka, C. Gentilcore, G. Kilaz, and N.-H. L. Wang, “Low-pressure hydrothermal processing of mixed polyolefin wastes into clean fuels,” *Fuel*, vol. 294, p. 120505, 2021.
- [44] W.-T. Chen, K. Jin, and N.-H. Linda Wang, “Use of Supercritical Water for the Liquefaction of Polypropylene into Oil,” *ACS Sustain Chem Eng*, vol. 7, no. 4, pp. 3749–3758, Feb. 2019, doi: 10.1021/acssuschemeng.8b03841.
- [45] P. Zhao *et al.*, “Supercritical water co-liquefaction of LLDPE and PP into oil: Properties and synergy,” *Sustain Energy Fuels*, vol. 5, no. 2, pp. 575–583, 2021.
- [46] S. Hongthong, H. S. Leese, and C. J. Chuck, “Valorizing Plastic-Contaminated Waste Streams through the Catalytic Hydrothermal Processing of Polypropylene with Lignocellulose,” *ACS Omega*, vol. 5, no. 32, pp. 20586–20598, Aug. 2020, doi: 10.1021/acsomega.0c02854.
- [47] “KMK Health and beauty supplies .”
- [48] D. J. C. Stewart, L. v. Fisher, M. E. A. Warwick, D. Thomson, and A. R. Barron, “Facemasks and ferrous metallurgy: improving gasification reactivity of low-volatile coals using waste COVID-19 facemasks for ironmaking application,” *Sci Rep*, vol. 12, no. 1, Dec. 2022, doi: 10.1038/s41598-022-06691-w.
- [49] R. Piñero-Hernanz *et al.*, “Chemical recycling of carbon fibre composites using alcohols under subcritical and supercritical conditions,” *J Supercrit Fluids*, vol. 46, no. 1, pp. 83–92, 2008.
- [50] H. Jin, B. Bai, W. Wei, Y. Chen, Z. Ge, and J. Shi, “Hydrothermal liquefaction of polycarbonate (PC) plastics in sub-/supercritical water and reaction pathway exploration,” *ACS Sustain Chem Eng*, vol. 8, no. 18, pp. 7039–7050, 2020.