

Research Article

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Hydrogen Production from Catalytic Polyethylene Terephthalate Waste Reforming Reaction, an overview

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Abstract: As a sustainable and renewable energy carrier for transition, hydrogen is considered as a key future fuel for the low carbon energy systems. During the past few decades, attention has been given to the conversion of waste materials, including plastics to the production of hydrogen. Studies in this field are of great importance because they resolve numerous problems brought about by plastic waste with other forms of waste. Polyethylene terephthalate (PET) is one of the major products of plastic waste which constitutes a major threat to environmental conservation efforts and harms living organism. Phenol has been chosen in this study as a solvent for PET to produce hydrogen because of unwanted liquid product in the bio-oil. This research investigates catalytic steam reforming of phenol with dissolved PET for hydrogen production. The aim of this study was the review of a highly active and stable catalyst for hydrogen production from steam reforming waste products. The analysis of product composition indicated that steam reforming of PET-phenol generally produced a high amount of aliphatic branched-chain compounds, together with a moderate amount of cyclic compounds. The reaction conditions also led to the alkylation of phenol by the reforming products from the PET-phenol solution with and without the catalyst. In conclusion, this study explored new ways to use 1 product derived from waste plastic materials. It provides a promising clean technology, which employed

polyethylene terephthalate waste dissolved in phenol (as a solvent) for hydrogen production.

Keywords: Hydrogen; catalytic; polyethylene terephthalate (PET); phenol; bio-oil; plastic; dissolution; waste; reforming; reaction.

1 Introduction

The USS light motor vehicle marine is above 225 million, daily travelling of above 7 billion miles, and regular consumption of 8 million barrels of oil [1]. The total imported petroleum is estimated to increase to 60% in 2025 with the knowledge that it is the third-biggest oil producer in the world. Attention was given to improving alternative fuels which run our society due to the first oil embargo in the 1970s [2]. Additionally, petroleum consumption poses momentous ecological concerns. Contaminants could be plentiful to influence community health and/or the surroundings in regions where 50% of Americans living as recent investigation expected. There has been an attempt to expand energy resource to overcome these concerns, especially in transference and in the discovery of cleaner fuels. One instance may choose ethanol another may select biodiesel, methane or gasoline due to the unavailability of alternative fuels. For an effective process, the majority of these fuels needs a diverse machine technology; nevertheless, hydrogen as a universal fuel can be manufactured from all of these contributing sources. Hydrogen is the most abundant element on Earth and is found as the primary element in the main-sequence stars and interstellar gas. The contrast of the main attributes for H_2 and other fuels are listed in Table 1.

For the low carbon energy systems of the future hydrogen is seen as a basic of coming fuel due to two reason; (i), water is the only yield of combustion and (ii),

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Table 1: Contrast of main attributes for H₂ and other fuels [3].

Fuel type	Energy per unit mass (J/kg)	Energy per unit volume (J/m ³)	Motivity factor	Specific carbon emission (kg C/kg fuel)
Liquid hydrogen	141.90	10.10	1.00	0.00
Gaseous hydrogen	141.90	0.013	1.00	0.00
Fuel oil	45.50	38.65	0.78	0.84
Gasoline	47.40	34.85	0.76	0.86
Jet fuel	46.50	35.30	0.75	-
LPG	48.80	24.40	0.62	-
LNG	50.00	230..	0.61	-
Bio diesel	37.00	33.00	-	0.5
Natural gas	50.00	0.04	0.75	0.46
Methanol	22.30	18.10	0.23	0.5
Ethanol	29.90	23.60	0.37	0.5
Charcoal	30.00	-	-	0.05

it has the power to decrease our demand on fossil fuels powerfully. For instance, H₂ has been known to generate power and to transport fuel. The power generated from hydrogen fuel cells and hydrogen-fueled turbines has the capacity to deliver a clean resource of energy production. Hydrogen-fueled vehicles would produce zero carbon secretions where the H₂ is burned directly or through fuel cell equipment. Nevertheless, the advantages of hydrogen fuel cell knowledge come with the resource of the generation process for the H₂. Presently H₂ is heavily manufactured either from fossil fuel resources such as naphtha, natural gas, and coal or through photolysis, water electrolysis or thermolysis. However, fossil fuels need high inputs of energy throughout the process which yield a high amount of CO₂ due to high temperatures. This becomes increasingly important considering the nearby hydrogen-based alternate feedstocks [4].

Increasing markets and energy safety have made the development of hydrogen technologies a global issue. A synopsis of how to improve the production of hydrogen technologies is illustrated in figure 1 which shows the theoretical flow sheet of this technology. Hydrogen from alternative sources such as biomass and water and, H₂ production via fuel processing technologies are the two areas that are observed [5].

Fuel cells is a new way to harness worldwide energy. They are ecologically noiseless, clean, and effective capable devices for electrical power production which use H₂ as their feed source. The current methods for generating hydrogen require high-temperature steam

feeding from non-renewable hydrocarbon, even though H₂ fuel cells have a small influence on the surroundings [6, 7]. Once H₂ is generated from renewable resources, such as, biomass and solar power, the complete ecological advantage of making power from hydrogen fuel cells is accomplished. Biomass and biomass waste to produce H₂ is a way to reduce fossil fuels usage.. Nevertheless, because methods such as steam reforming of bio-oils, enzymatic decomposition of sugars, and gasification travail from small hydrogen generation ratios and multipart treating desires, conversion of biomass to hydrogen remains a challenge.

The hydrogen economy is a hypothetical future economy in which hydrogen is produced, stored and delivered to be a replacement of fossil fuels in the transportation sectors. With the onboarding of hydrogen fuel cell technologies, zero-emissions can be achieved from the vehicle operation itself [8]. A 'hydrogen economy' is composed of five segments: hydrogen production, storage, delivery, conversion, and end-use applications. Fossil fuels, electricity and nuclear energy can be utilized to generate hydrogen through chemical, electrolytic, thermal and photolytic processes [9]. Energy security, urban air pollution, air pollution health effects and global warming are the major factors to promote the hydrogen economy. Currently, most of the industrial countries' economies have become more dependent on fossil fuels. From 1990 to 2007, the energy demand in Canada increased by 26%, and about 30% of the total energy was consumed by the transportation sector [10].

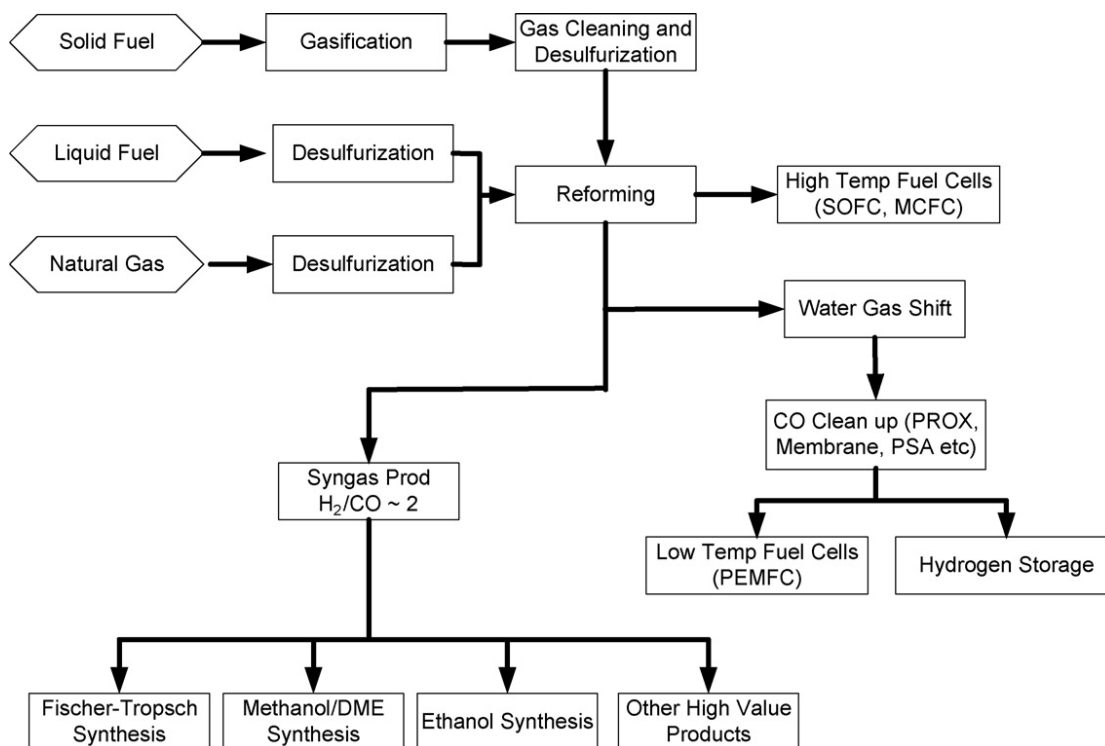


Figure 1: Fuel treating of gas, solid, and liquid fuels for hydrogen generation [5].

The extraction of hydrogen sources, the hydrogen production, the hydrogen storing, the transference and usage of hydrogen are five critical units that should be included in a comprehensive hydrogen energy system. Yet, up to now, a plan to store hydrogen has not advanced economically to be a viable renewable energy resource. So far, the knowledge to store hydrogen has been stated in numerous works. Even though resources have improved, several features, for instance, safety, increasing the gravimetric density, energy effectiveness, volumetric density, etc. require further consideration. Hence, to improve the new hydrogen storing system with adequate storage capacity and moderate operational condition is the big challenge of the critical application of hydrogen [11, 12].

For planning purposes, there needs to be a safety standard in place that is equal to traditional fuel safety measures concerning flammability, density. the gaseous formal of the fuel at ambient circumstances in composition with the extensive flammability, small density and disappearance of the gas in addition to its flames need modified processes [13]. The alteration of resident codes and abiding by acceptable levels for hydrogen plants require challenging safety measures.[14]. Different safety-relevant attributes of H_2 and other fuels are revealed.

2 Production of Hydrogen

Fuel cell usages are the anticipated grown claim for hydrogen which commands the improvement of first-hand ways mainly from renewable feedstocks for hydrogen generation. Carbon dioxide is extricated from the air through biofuel alteration and can be absorbed in the progress of biomass, the consumption of biofuels for hydrogen generation has the important benefit of being CO_2 inherent over dissimilar methods such as partial oxidation (PO), steam reforming (SR), etc. [15].

The method of steam reforming conducted at high temperatures, generally from 700 to 1000 °C, ; the vapor responds to the fossil fuel at this high temperature. The steam reforming method in contrast to POX and ATR has a lower operational heat and produces reformat with excellent H_2/CO ratio (3:1); plus, it does not require oxygen. For hydrogen generation, steam reforming is generally applied in the industry because of its high thermal efficiencies that reach more than nearly 85%, in terms of higher warming values. To begin the reactions, steam reforming needs energy input, and it is an endothermic method in the nonexistence of oxygen gas [5].

H_2 is mainly formed by catalytic steam reforming natural gas, naphtha or light hydrocarbons. Recently researchers have focused on H_2 production from biomass.

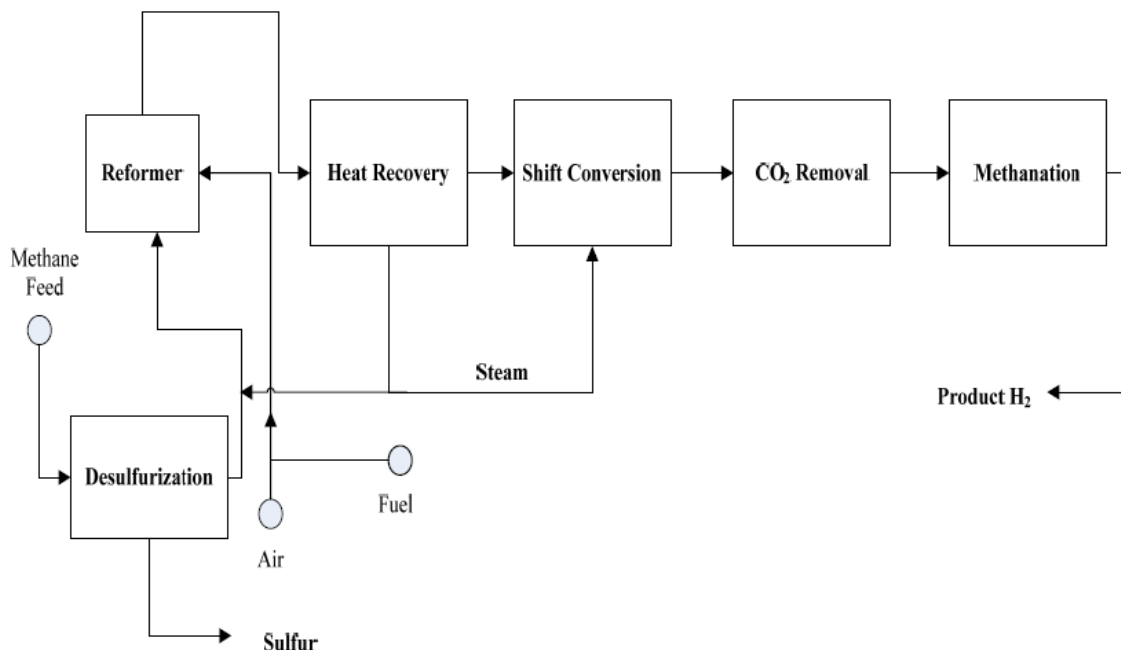


Figure 2: Simplified Flow Diagram of Steam-Methane Reforming Process [17].

Biomass as a renewable energy resource has qualities of clean energy which is CO₂ neutral, cost-effective and has low sulfur content. Catalytic steam reforming of bio-oil and steam gasification of biomass are two leading technologies for the production of hydrogen from biomass that have been explored. One alternative solution for bio-oil utilization is steam reforming of bio-oil for hydrogen generation [16]. As an example for steam reforming, in Figure 2, natural gas passes through the desulfurization unit to reduce the catalytic sulfur compound level and then is fed into the reformer to react with the superheated steam at 750-800°C [9].

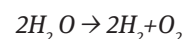
Currently, hydrogen can be produced from coal, natural gas, and oil, which are non-renewable resources [18]. It can be made from a variety of sources. Almost half of the hydrogen currently produced is obtained from catalytic gasification and thermal processes using natural gas as feedstock, whereas the second largest source is naphtha and heavy oils [19]. Table 2 depicts the summary of hydrogen production technologies. The steam reforming of hydrocarbons is the dominant efficient technique compared to others. Hydrogen production from a non-renewable and temporary source such as natural gas has the lowest cost compare to bio-oil. Nevertheless, natural gas is a limited fossil fuel that will eventually become too expensive to extract and eventually will be depleted.

3 Bio-processes for hydrogen gas production

Main bio-processes used for the production hydrogen can be categorized into three groups; water bio-photolysis by algae, hydrogen production of dark-fermentative and dark/photo-fermentation hydrogen production [21, 22]. The use of these methods presents several advantages since they are abundant renewable non-food materials and do not compete for agricultural crops.

3.1 Bio-photolysis

Photosynthetic production hydrogen from water is a biological process that can convert sunlight into beneficial and stored chemical energy by the following general reaction:



Green algae, under anaerobic conditions, can either use hydrogen as an electron donor in the CO₂-fixation process or evolve hydrogen. Hydrogen production by green microalgae requires a few minutes to hours of anaerobic development in the dark to induce the synthesis and activation of enzymes involved in hydrogen metabolism,

Table 2: Summary of hydrogen production technology [20].

Technology	Feedstock	Efficiency (%)	Maturity
Steam reforming	Hydrocarbons	70-85%	Commercial
Auto-thermal reforming	Hydrocarbon	60-75%	Near term
Biomass gasification	Biomass	35-50%	Commercial
Electrolysis	H ₂ O + electricity	50-70%	Commercial
Photolysis	H ₂ O + Sunlight	0.5%	Long term
Thermochemical water splitting	H ₂ O + heat	NA	Long term

* Hydrogen purification not included

including a reversible hydrogenase enzyme. The *hydrogenase combines protons (H⁺)* in the medium with electrons (donated by reduced ferredoxin) to form and release hydrogen. Thus, green microalgae possess the genetic, enzymatic, metabolic, and electron-transport machinery to photoproduct hydrogen gas. The synthesis of hydrogen permits sustained electron flow through the electron-transport chain, which supports the integration of ATP.

3.2 Dark-fermentative hydrogen production

Biohydrogen production through a dark fermentation (DF) process has gained increased attention in recent years, mainly due to process simplicity and the possibility to convert a wide range of substrates. Moreover, hydrogen gas presents a high-energy yield (122 kJ g⁻¹); its combustion generated the only water vapor, and its surplus can be stored and used when needed [23]. In this technique, diverse microbial organisms are employed to hydrolyze the diversity of polymeric carbohydrates to form hydrogen and other products like butyric, lactic, acetic acids, etc. [24]. Hypothetically, a maximum of 12 mol of hydrogen can be found from the complete oxidation of one glucose mole. The amount of hydrogen production by dark fermentation highly depends on the pH value, hydraulic retention time (HRT) and gas partial pressure.

Nevertheless, only four hydrogen mol can be achieved per glucose mole through the dark fermentation method with acetate and CO₂ as the other fermentation end products and this yield are obtained when the partial pressure of hydrogen is kept adequately low [25]. Because solar radiation is not a requirement, hydrogen production by dark fermentation does not demand much land and is not affected by the weather condition. Hence, the feasibility of the technology yields a growing commercial

value. In another study, biohydrogen was produced from industrial beverage wastewater under different experimental circumstances, firstly by using pure cultures of *Escherichia coli (XL1-Blue)* and *Enterobacter cloacae (DSM 16657)*, which resulted into remarkable increase in hydrogen production. To further clarify the particular reasons beyond the observed improvements in hydrogen generation, experiments were carried out with only *E. coli (XL1-Blue)* and nitrogen sources such as yeast extract and tryptone supplementation. The result of these tests was that both the applied nitrogen sources and the *organism (E. coli)* could independently improve hydrogen production. However, the most astounding increase occurred when they were utilized together with an optimal initial wastewater concentration determined as 5 g/L [26].

3.3 Photo-fermentation hydrogen production

Photo-fermentation hydrogen production is an extremely encouraging method due to the mild reaction conditions, high hydrogen production, use of solar energy and conversion of organic waste to hydrogen. Photosynthetic bacteria play a vital role in the photo-fermentation process, and their performance determines the utilization range and conversion efficiency of the substrate to hydrogen. Thus, the screening of bacteria with a remarkable capacity for hydrogen production is crucial to the photo-fermentation hydrogen production process [27]. However, these processes have three main drawbacks: (i) use of nitrogenase enzyme with high-energy demand, (ii) low solar energy conversion efficiency and (iii) application for elaborate anaerobic photobioreactors covering large areas. Hence, at present, the photo-fermentation process is not a competitive method for hydrogen production.

3.4 Dark/photo-fermentation

A combination of processes of dark fermentation and photo-fermentation is an exciting approach for the maximum conversion of energy from carbohydrate-rich substrates [28]. Using this method, a maximum yield of 14.2 mol H₂/mol sucrose was achieved by utilizing *Clostridium pasteurianum* and photosynthetic bacteria of *Rhodospseudomonas palustris* WP3-5 [29]. When the two systems are combined, the low molecular weight organic acids formed as intermediates from anaerobic fermentation of carbohydrates (or organic wastes) are further used by the photosynthetic bacteria to produce H₂ in a photobioreactor.

4 Biomass to Hydrogen

Bio-oil over a knowledge that named fast pyrolysis of biomass can be manufactured.

For the commercialization of hydrogen production, pyrolysis and gasification are perceived as the greatest average-term knowledge from biomass; however, biomass gasification is a research and development area that is shared between hydrogen and biofuels production. Figure 3 shows a classic flow sheet for the production of hydrogen from biomass. The drying of biomass might not be acceptable based on its energy demands. Hence, other ways are being looked at in terms of wet biomass as well.

The feedstocks of biomass with incompatible fineness and meagre fineness control are untreated yields. In line with climatic differences, product sort, and position, the generation procedures are variable. Meanwhile less homogenous and low fineness fuels require further complex alteration systems, erratic fuels have helped to the troubles in technical novation. To yield additional stable and more excellent- fineness fuels that can be explained by modern standards, there is a necessity to justify the generation and procurement of fuel. Slighter plants desire to need upper levels of fuel fitness and better fuel identity, whereas critical systems need to be appropriate for lower fitness and inexpensive fuels. Therefore, particular endurance that each knowledge can reclaim, and well thought of this relation, is desired [30].

To develop the finances for generation procedures and the preparation of treatment of a biomass feedstock, multiple improvements are desired:

- Classifying the features of feedstocks and feed procurement that will permit the knowledge to improve.

- Gasification of biomass which is connected to overall biomass and renewables directions and exploration and not special for hydrogen.
- Raw gas management and purification.
- Joining subjects and system accretion. Moreover, one should expect endurance that can be compatible with the particular knowledge and consider the link between the generation standard and fuel fitness demands.

Fossil sources (natural gas and coal), and renewable sources, like biomass and water with input from renewable energy bases like wind, sunlight, hydro-power or wave, are a diversity of feedstocks that hydrogen can be formed from them. Chemical, biological, photolytic, thermo-chemical and electrolytic are a diversity of procedure knowledge that can be applied in this area and each technology suggests single advantages, difficulties and chances and also they are in an unlike phase of improvement. There are some terms that will affect the selection and scheduling of the different choices for hydrogen generation which are the puberty of the knowledge, marketplace uses and claim, local accessibility of feed, strategy matters, and fee. Figure 4 stated a summary of the different feeds and procedure knowledge.

4.1 Centralized Hydrogen Production

Hydrogen production can be theorized a marketable knowledge for artful aims from all fossil energy bases; however, it is not yet have efficient marketability. Even though the hydrogen production cost of natural gas in average-sized plants could be decreased, hydrogen production on a larger scale has the capability to be comparatively low in cost. Since CO₂ storing capabilities are not entirely technically and commercially resolved, decarbonizing the hydrogen production process is a significant problem. In addition to admission for CO₂ saving research and development needs to occur regarding the absorption or separation procedures; furthermore, it is vital to decrease capital fees, rising plant viability and utilizing pliability and develop authenticity. Figure 5 stated a standard plan of hydrogen delivery from a natural gas-based localized hydrogen generation plant [30][32].

For gas separation to detach hydrogen or CO₂ from gas mixes and for hydrogen purification to generate H₂ proper for fuel cells, further research and development are mainly required which includes the adsorption ingredients, improvement of catalysts and gas separation membranes for the generation and filtration of hydrogen.

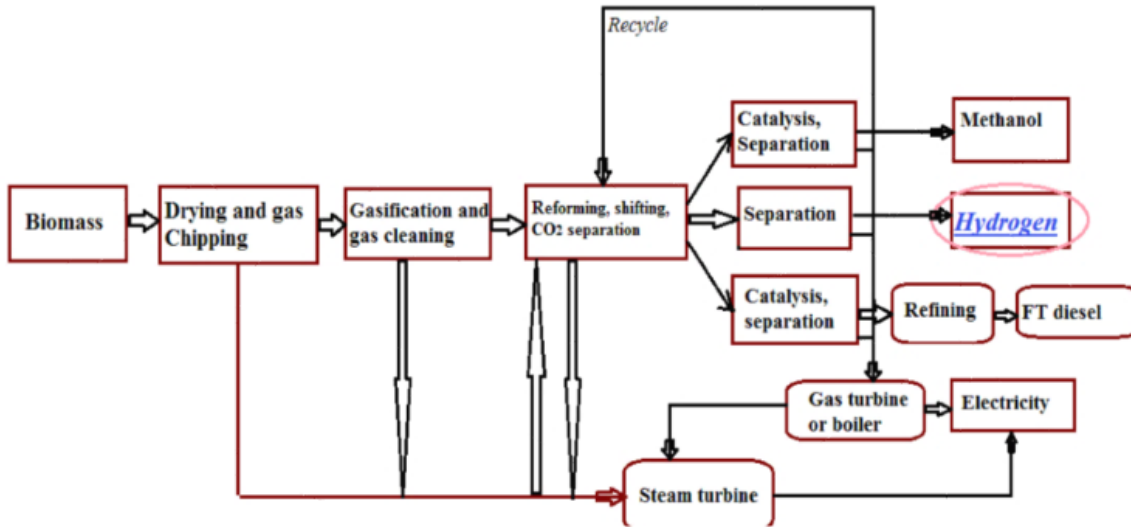


Figure 3: General flow sheet for hydrogen, methanol or FT diesel generation through biomass gasification [30][32].

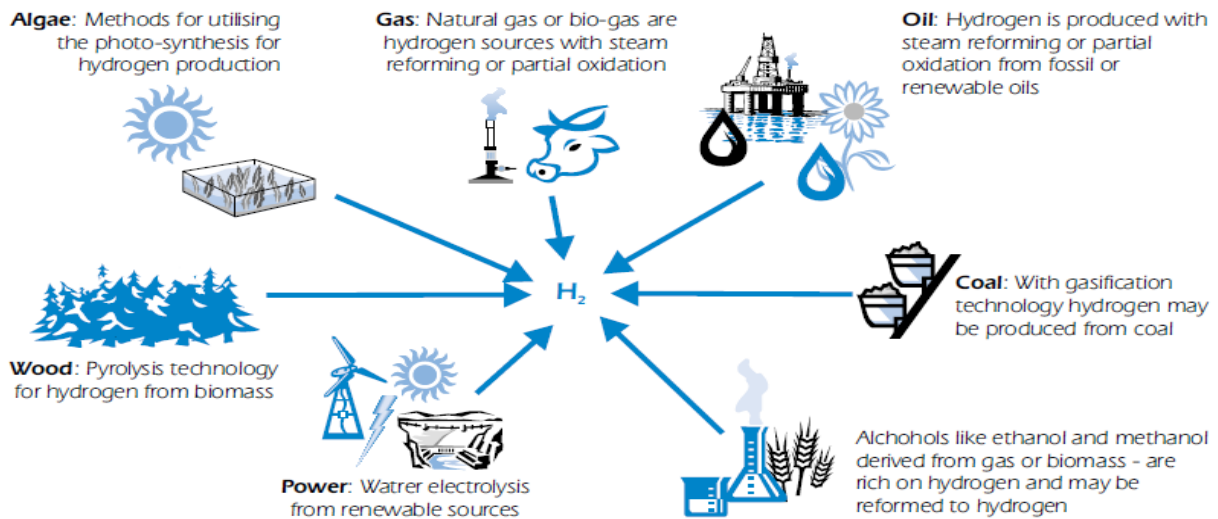


Figure 4: Various feed and procedure alternatives for hydrogen [30][32].

Hydrogen could also junction electrical energy in the coming as a vital energy vector which stores, transfers, and transports energy in a usable form to customers. Hydrogen opposite to renewable energy bases which cannot yield energy every time can hold and keep this energy till it is required and can be conveyed to where it is wanted.

Overall, the production of hydrogen can be from:

- Reforming liquid biofuels like ethanol cellulosic or butanol at the fueling station.
- Gasifying biomass at a local capital with channel repartition of hydrogen- periodic which divided hydrogen.
- Production by applying the digester gas from the agricultural site or animal waste or from handling plants of wastewater or from landfill gas.
- Volatilizing coal at an integrated gasification composed phase (IGCC) plant with carbon capture and storage (CCS).
- Electrolyzing water applying zero-carbon electricity bases like nuclear and renewable energy.

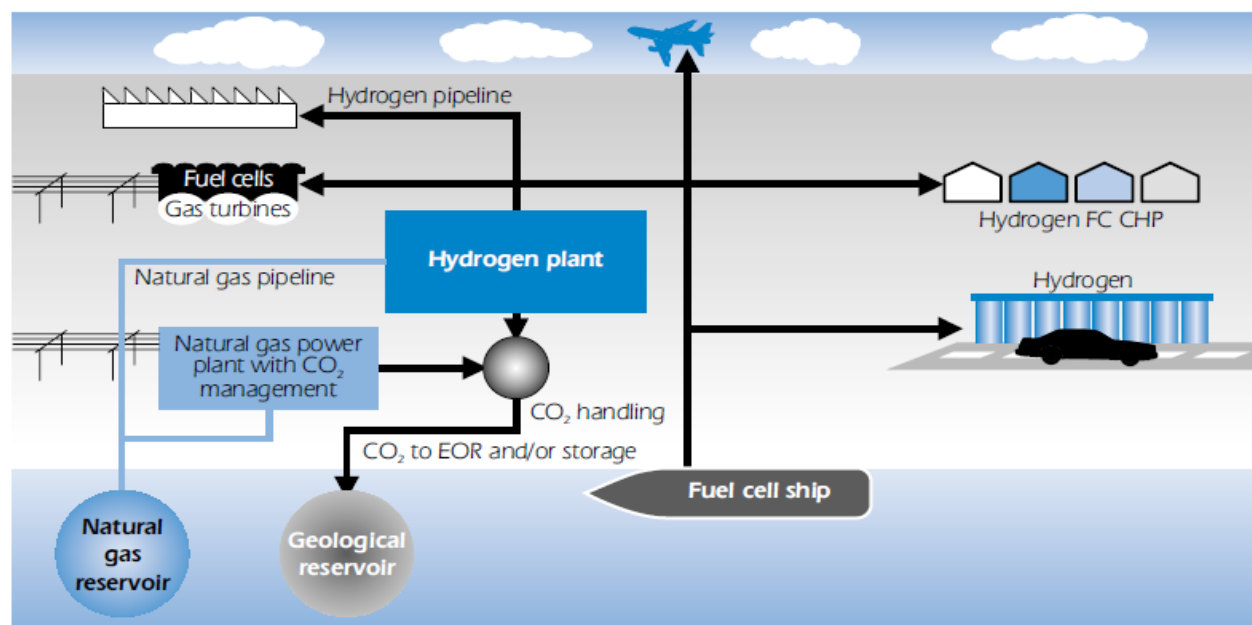


Figure 5: Standard outline for big-scale localized hydrogen generation with CO₂ capture [30].

4.2 Phenol as a Source of Hydrogen

Several oxygenated compounds such as ethylene glycol, acetol, acetone and also more massive aromatic such as phenol, xylene, and even glucose have been tested as model compounds. The coking trend, with acetone exhibit, the maximum one is comprised of the striking difference in the performance of these light components [31][33]. Phenols performance under reforming conditions has also been investigated, and is reflected as the components lignin depolymerization resultant. The best active catalyst is based on Rh over mixed metal oxide of Mg, Ce, and Zr [32][34]. The high S/C ratio (>10) (that is necessary to be used to avoid extensive coking) is one of the characterizations of phenol. The complete conversion of phenol and 90% of hydrogen yield can be achieved at 700 °C of stoichiometric temperature. Coking of the catalyst resulted in the deactivation of the catalyst. The presence of the aromatic ring, which is very prone to coking, is the reason for this.

The subsequent reaction system can be measured to define the phenol steam reforming reaction with regards to the works of literature [33-35]:



5 Plastic Waste as a Feedstock for Hydrogen Production

5.1 Plastics to Hydrogen

Chemical recycling of the waste plastics, by pyrolysis and gasification, is a familiar way to produce valuable hydrocarbons. The plastics gasification yields a syngas which has a high value of H₂. Hydrogen as a fuel could show a significant role as the incoming energy source. Consequently, hydrogen generation from the plastics gasification characterizes a range of active exploration. Furthermore, compared to biomass or some other municipal solid wastes, the plastics have an upper heating value and H₂ content which guarantees a high hydrogen generation from the gasification of plastics [36][38].

Waste plastic is one this feedstock resource for the generation of hydrogen where, perhaps, employing gasification–big pyrolysis molecules of the plastic can be decomposed to generate hydrogen. Around 13 million tonnes of waste plastic through Western Europe was produced in 2004. Nevertheless, the recycling level for the plastic was low than 10%, demonstrating a waste of a valued source. Moreover, for waste plastic, the recycling knowledge attracted towards the small grade, for instance, HDPE are reprocessed as pipes, dustbin sacks and garden furniture; PVC is reprocessed for shoes, sewer pipes, electrical fittings, and flooring. Processing

uses for mixed post-consumer plastic waste contain plastic fencing, plastic lumber, industrial plastic pallets, and traffic cones. As a result, generating hydrogen from plastics economically and environmentally is a favourable knowledge; nevertheless, the practical difficulty is to raise production performance of H₂ from the gasification of plastic waste. The use of catalysts is the main issue in maximizing hydrogen production from waste plastics by pyrolysis–gasification [4].

5.2 Generation and Quantities of Plastic Solid Waste (PSW)

Plastics are an important part of everyday life.. Every home has an abundant amount of plastics to enhance the quality of life , from clothing, packing, applications, vehicle, and electrical devices, to artful uses, insulations, aerospace, automotive slices, greenhouses, and mulches. Polymerization and plastic alteration impacts each economy. During 2000, the UK employed about 4.5 million tons of nearby generated plastic and 4.68 million tons throughout 200, which represent 7.5% of the UK request for chemicals in 1998. Figures 6 and 7 demonstrate the UK marketplace usage by division and polymer category in 2007, respectively [37][39].

5.3 Polyethylene Terephthalate (Pet)

Apart from plastic consumption, PET had chosen in this study since it is soluble in phenol [38][40][40] which can make a unique product that contains two main waste component (phenol+PET) in the world. Poly (ethylene terephthalate) (PET) with the formula of (C₁₀H₈O₄)_n, one of the conventional linear thermoplastics used extensively in fibres, films, and soft-drink bottles is the main contributor to municipal waste [39][41][41]. Polyethylene terephthalate (PET) for beverages has become the most promising packing material internationally. The outstanding material properties of the PET material is the cause for this progress, especially it’s non-breakable and the deficient weight of the bottles compared to glass bottles of the same filling volume. Nowadays, PET bottles are used for soft drinks, mineral water, energy drinks, iced teas as well as for more sensitive beverages like beer, wine and juices [40][42]. PET organizes a momentous fraction of the curbside mix and represents a critical recycling opportunity [41][43]. Poly(ethylene terephthalate) (PET) resin is cheap, light, transparent, sturdy, and easy to

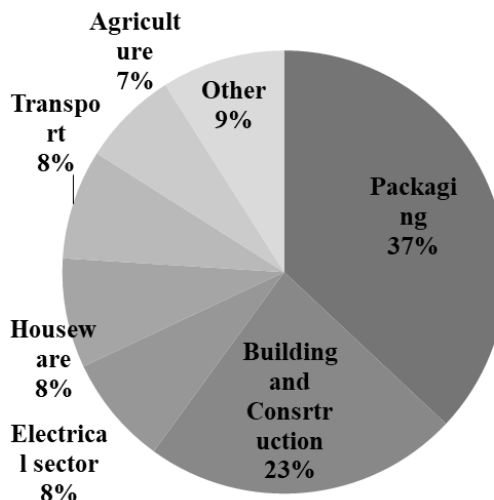


Figure 6: UK average plastic usage by marketplace division [37][39].

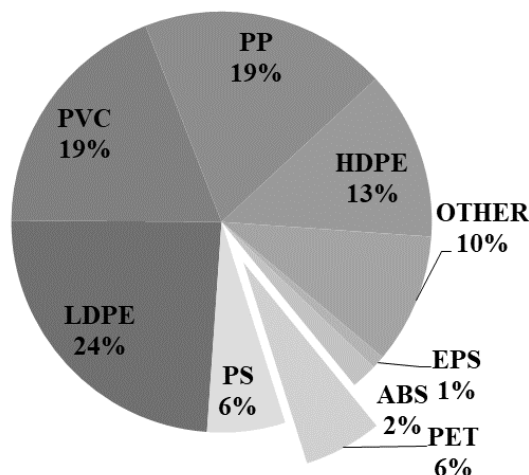


Figure 7: UK average plastic usage by polymer category. Other contain: POM, PC, PA, PC/ABS, PBT, PMMA, PUR, UPR [37][39].

process and, consequently, is used not only in several industries but also in daily life [42][44].

For a long time, a bottle-to-bottle reprocessing of post-consumer PET packaging materials was not possible, due to being uninformed about the pollution of packaging polymers during first use or recollection. In 1991, the first food contact approval of post-consumer PET indirect food contact applications had been given for post-consumer recycled PET in the USA. Now, 20 years after the first food approval of a PET super-clean recycling process, Welle, provides an overview of the worldwide development of the bottle-to-bottle reprocessing of PET beverage bottles, e.g. the recollection quantity of post-consumer PET bottles

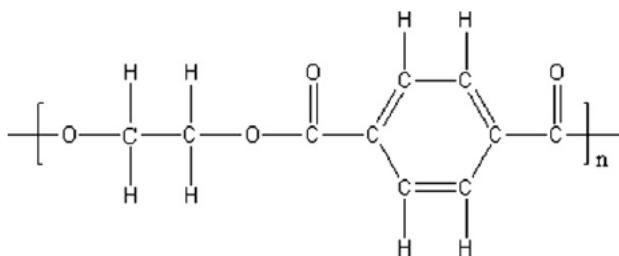


Figure 8: The molecular formula is $(C_{10}H_8O_4)_n$ or $C_5H_4O_2$ for short [44] [46][46].

and the super-clean recycling technologies [40, 43]. The molecular structure of PET is shown in Figure 8.

PET is less susceptible than polycarbonate: PET cannot record tracks of α -particles. Thus, PET is often used to selectively record heavy-ion tracks in the surroundings where serious α -particles exist. Its charge and mass resolutions for numerous MeV/amu Ne ($Z = 10$) to Si ($Z = 14$) ions are suitable for the measurement of track factors; hence, it was one of the detectors used in the discovery of cluster radioactivity. PET track detectors have also been used broadly in many fields, such as substantial cosmic-ray analyses, nuclear track membranes, nano- and microstructure device manufacture, and anti-counterfeiting methods [44][46].

PET bottles are considered by low weight, high strength, and small permeability of gases (mainly CO_2) along with by their aesthetic appearance (excellent light transmittance, smooth surface). A very significant characteristic of PET, decisive in the choice of its full application in the manufacture of packaging for the food industry, is that it does not have any side effects on the human organism. PET does not create a direct threat to the surroundings, but owing to its substantial fraction by volume in the waste stream and its high persistence to the atmospheric and biological agents, it is seen as a harmful material [45][47].

The recycling of waste polymers, including PET can be carried out in many ways. A beautiful form of recycling of used polymer materials is the so-called, “materials recycling”, which consists of the collection, disintegration, and granulation of waste polymer and then their recirculation into production. This PET recyclate can be used to make products which do not have to meet very high-quality standards. For many reasons, this form of recycling can be effectively applied only to a part of all-polymer wastes. The availability of a wide spectrum of degrading (depolymerizing) agents and a large variety of products, e.g., monomers for polymer and resin syntheses and other additives for polymeric materials, are some of

the advantages of PET chemical recycling. Therefore, in recent years one can observe a growing interest in the use of PET waste for low-tonnage production of specialized products such as raw materials for the syntheses of saturated and unsaturated polyesters, polyurethanes, coating materials and additives [45, 46].

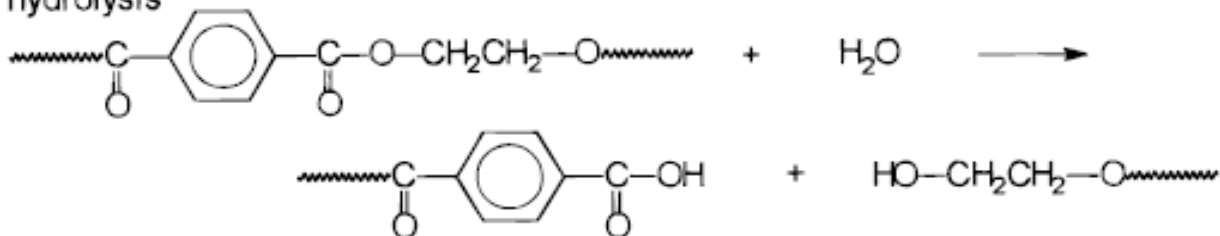
Currently used PET is recycled chemically by solvolyses such as methanolysis [47][49][49] and glycolysis [48, 49] [50, 51][50, 51]. In these methods, PET is converted to dimethyl terephthalate (DMT) and ethylene glycol (EG) and a monomer such as dihydroxyethyl terephthalate (DHET) and a low molecular- weight oligomer. Terephthalic acid (TPA) and EG can be obtained by hydrolysis in acidic and basic conditions [50][52].

PET has high melt viscosity and therefore, low mobility, which is a disadvantage for processing. One of the essential approaches to solve this problem is to formulate the composites of PET with polystyrene (PS). PET films can be swollen by $SC\ CO_2$. Based on this fact, Dan Li have prepared PET/PS composite films. The monomer of styrene and initiator were absorbed by PET film with the aid of $SC\ CO_2$, and then the monomer was polymerized to obtain binary blend films [51][53].

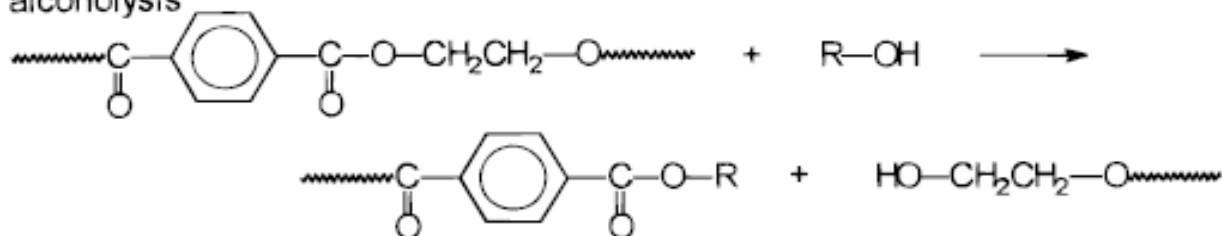
Paszun and Spychaj [45][47] conducted an extensive review of the state of PET chemical recycling. They classified the methods into six categories: methanolysis, glycolysis, hydrolysis, aminolysis, ammonolysis, and others which show in Figure 9. Efforts are still continuously being made to develop new or modified methods for the chemical recycling of PET to produce raw materials and ingredients for various chemical products. In addition to the conventional systems, post-consumer PET has been treated by sub- and supercritical methanol and water to recover the monomers of terephthalic acid (TPA) (or dimethyl terephthalic ester in methanolysis) and ethylene glycol (EG). While all of these methods have advantages, the disadvantages include harsh reaction conditions of high temperature and high pressure, the use of complex mixtures of degrading reagents or additives, difficulty in the separation/purification of solvent recovery or products, and low yields of the desired monomers. Among the various chemical recycling methods, ammonolysis and aminolysis are attractive for degrading PET due to the high reactivities of ammonia and amines toward polyesters. In ammonolysis/aminolysis methods, the main objective is to obtain amide compounds from PET for use as coating materials, plasticizers, and ingredients. However, these methods have not yet been employed in industrial processes, and studies on them are limited even though they have been investigated since the 1960s. Most initial aminolysis studies focused on the surface morphology or

groups:

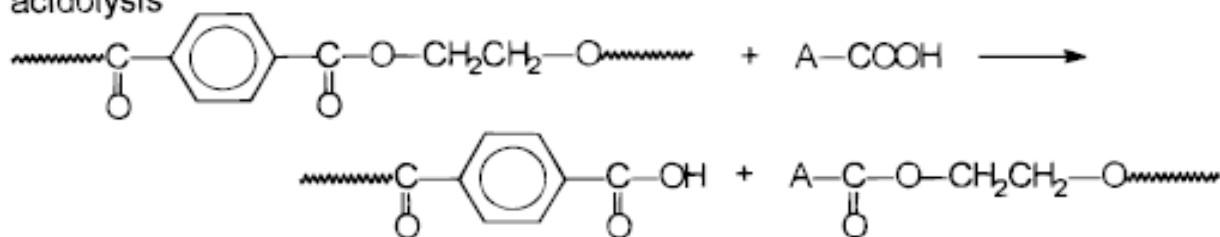
hydrolysis



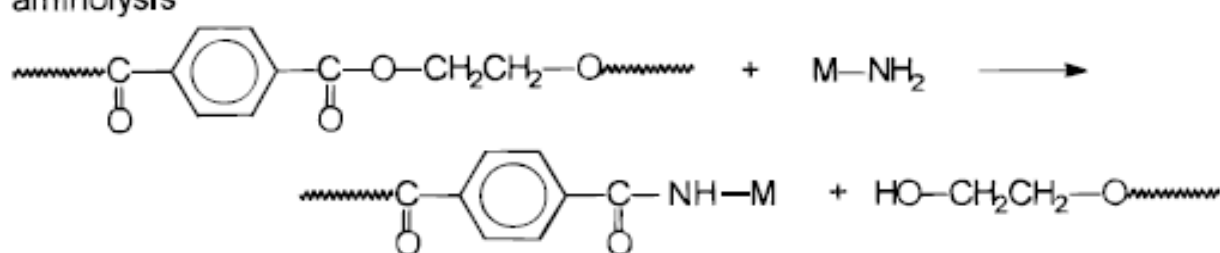
alcoholysis



acidolysis



aminolysis



(4)

Figure 9: Schematic of PET chemical recycling methods [45][47][47].

modification and the strength of PET fibres, and data on reaction rates and monomer yields are scarce. Therefore, ammonolysis/aminolysis methods are not considered to be suitable for recovering TPA and EG monomers from PET [52][54]. Mormann [53][55] studied the ammonolysis of various polymers including PET with sub- and supercritical ammonia (critical temperature of 405.6 K and critical pressure of 11.3 MPa) containing water, which converted majority of the PET into terephthalamide and EG [52][54].

5.4 Dissolution/Reprecipitation (Dr) Technique

Currently, the investigations regarding the dissolution/ reprecipitation (DR) technique are limited to the recycling of low-density polyethylene (LDPE), high-density polyethylene (HDPE), and polypropylene (PP). The application of this technique has been a success at as a pilot, but further use at a regular recycling plant scale has

yet to be researched. Selective dissolution precipitation (SDP) method was developed based on DR technique in plastic recycling. The advantages of using SDP include:

- a. Dissolution of plastic waste in the solvent increases its bulk density, hence reduce the volume of the waste to be treated.
- b. The plastic waste is converted to grains or powder at the end of the process, which is suitable to be sent into the following processing units.
- c. The contaminants (labeling, dyes, etc.) can be removed during the dissolution stage. During the recovery of solvents using the drying method, these compounds can be collected for disposal or reuse if necessary.
- d. As the recycled plastic has quality and structure comparable to their virgin materials, they can be mixed for the production of new materials.
- e. Less effort is needed to manually separate the plastic waste to different types, as DSP method achieves the plastic separation based on the principle that different plastic dissolves in a solvent at different temperature. By carefully controlling the temperature, solutions containing various dissolved plastics can be obtained from municipal plastic waste.
- f. There is a lot of plastic waste made by the combination of more than one plastic resin; and this waste requires extra effort to be separated mechanically. (for example, certain HDPE bottles that have caps or plastic labels which are made of LDPE) and can be automatically separated by using SDP method. This solves the problem for mechanical recycling or even manual sorting that is usually used in recycling plants[54][56].
- g. The energy in terms of heat required for this process is less compared to other recycling methods like incineration, pyrolysis, gasification, etc. This means a great reduction in process operating cost.

However, before its application in the real recycling industry, several limitations have to be addressed, which include:

- a. Pretreatment is needed to clear the contaminants in the municipal plastic waste.
- b. As solvents are volatile, the SDP process has to be done using extra safety measures.
- c. As the research on this method is still limited, the reaction data and the kinetic models are not available yet, and this causes difficulty in the reactor design.

Extensive research has been conducted on the pyrolysis of waste plastic to study the production of renewable energy

from plastic waste. Although the investigations show the feasibility of the pyrolysis process to produce fuels, only a few methods have being commercialized in the plastic recycling plant. A significant cause is a difficulty to scale up the process into a continuous process, which is usually done in a typical plant. When heating above the melting point of waste plastic, the melted plastic can flow in the process units in liquid form. However, after shutting down the process, the unreacted plastic that exists in the pipelines between the process units gets cold and turns back into a solid form. Subsequently, the pipes are clogged, and they have to be heated before the next start-up of the process. Thus, a lot of pyrolysis processes are performed in the batch reactor. However, the dissolution/re-precipitation technique provides an insight into the development of the continuous pyrolysis process. The plastic to be pyrolyzed can be dissolved into the solvent, and several contaminants can be eliminated during the process. Next, instead of an anti-solvent addition and plastic extraction, the resulted solution can flow in the pipes into the next process unit at a temperature below the melting point of plastic, without the problem of clogging pipes. The solvent can then be recycled for repeated use, as is the case in the DR method. However, when considering the usage of dissolved plastic in the solution in the pyrolysis process, the possible reaction on the solvent has to be studied. This is important as the recycling of the solution is one of the critical features in the process to ensure its cost-effectiveness. Besides, the introduction of solvent into the pyrolysis reaction might produce an unwanted specific response. Besides, the concentration of plastic dissolved in a solvent might possess a maximum amount, or the resulting solution is too “sticky” to flow inside the pipes. Hence, these issues have to be checked to ensure the possibilities of implementing the method mentioned above.

6 Catalyst For Steam Reforming

Catalyst is a chemical substance that causes or accelerates a chemical reaction and modifies and increases the reaction rate without itself being affected and also without being consumed during the process, and it only alters the activation energy necessary to proceed in the reaction. Catalysts can be divided into two main types - heterogeneous and homogeneous. In a heterogeneous reaction, the catalyst is in a different phase from the reactants. In a homogeneous reaction, the catalyst is in the same phase as the reactants. In heterogeneous catalysis, metal oxides have various roles: as catalysts, as

support material for catalytically active metal particles, as promoters. Active metals are part of the catalyst which is particularly good at adsorbing reactants and helping them to react. Metals such as Ru, Rh, Pd, Pt, Ir (noble) and Ni, Co, Fe (non-noble) are catalytically active.

The catalyst support is a material, usually a solid with a high surface area, to which a catalyst is affixed. In multiphase catalysts, the active catalytic material is often present as the minor component dispersed upon support sometimes called a carrier. The support may be catalytically inert, but it may contribute to the overall catalytic activity [55, 56][57, 58][57, 58]. The reactivity of heterogeneous catalysts and nanomaterial-based catalysts occurs at the surface atoms. Consequently, considerable effort is made to maximize the surface area of a catalyst by distributing it over the support. MgO, Al₂O₃, La₂O₃, ZrO₂, CeO₂, and ZnO are examples of metal oxide supports.

6.1 Active Metal

Active metals are a collective name for metals that react strongly or quickly with other substances. The metals in the first column of the periodic table are very reactive with other elements because they have a single electron in their outermost shell, just waiting to be stripped off to form a complete crust in some other atom. Examples of active metals are Lithium, Sodium, Potassium, Rubidium, and Cesium, which are also known as the “Alkali” metals. Sodium and Cesium I have seen first-hand create explosive reactions with water -- they want to react so much with water molecules they will displace one of the hydrogens in the H₂O molecule to make NaOH, for example, emit hydrogen gas, which then burns (or explodes). Metals and other elements are characterized in their reactivity by their “electron affinity” or “electronegativity”. Co, Ni, Rh, and Pt are examples of these metals.

6.2 Nickel Based Catalyst

Nickel nitrate is a chemical combination Ni (NO₃)₂ or any hydrate of it, and it is a green monoclinic system crystal which is soluble in alcohol and somewhat soluble in acetone and simply solves in water. “Nickel nitrate” typically depends on nickel (II) nitrate hexahydrate since the anhydrous method is not generally encountered [57][59][59]. Several studies have revealed Ni as the most suitable metal [58-60][60-62][60-62] for steam reforming of ethanol. Ni-based catalysts are used in large scale reforming processes due to their cheaper and more

available nature than noble metals [61][63][63]. Ni shows an excellent performance for C-C breakage, as well as high rates of methanation [62][64].

Nevertheless, it is commendable that noble metals such as Rhodium (Rh), Palladium (Pd), Ruthenium (Ru), etc. are greatly more resistant, active and their use at high temperatures drops the inclination of coke formation in the catalytic surface [63-67][65-69][65-69]. Even though the noble metals are incredibly costly, it has been stated that inserting a small quantity of noble metallic to a non-noble metallic catalyst as a result of the spill-over influence the activity of the non-noble metal [66, 68][68, 70]. Recently, Pd-based catalysts have been widely investigated due to their lower cost and high performance in comparison to Pt-based catalysts [69-72][71-74].

6.3 Palladium Catalyst

On the one hand, Pd-based catalysts have been widely investigated recently because of its lower cost and superior performance compared to Pt-based catalysts [69-74]. Pd is another essential transition metal with high catalytic activity. In recent years, much attention has been focused on the high electrocatalytic activity for formic acid oxidation on Pd and Pd-based catalysts [71, 73-77]. Numerous researchers recently [76-83] have stated the Pd-based membrane reactor (MR) performance in the methanol steam reforming (MSR) reaction. For the steam reforming process, the active and stable catalysts for the dry reforming of methane (DRM) reaction are mostly precious metals, such as Rh and Pd, which are less prone to coke deposition and deactivation at high temperature [82][84].

6.4 Catalyst support

The most common supports that have been considered for the deoxygenation of phenolic compounds include acidic supports such as the reducible oxide supports first introduced in Section 2.2 and activated carbon. Of these supports, acidic supports such as Al₂O₃ and ZrO₂ have received a lot of attention.

A variety of authors have indicated that the combination of a noble-metal catalyst and acidic support can be very beneficial for the deoxygenation of phenolic compounds [83][85]. Contrary to the high interest in acidic supports, Al₂O₃ has recently been ruled out as viable support [84][86]. As mentioned earlier, bio-oil tends to contain a significant amount of water, and the catalytic

deoxygenation of phenols produces a considerable amount of water as well. In the presence of such a high amount of water, Al_2O_3 is converted into boehmite [$\text{Al}_2\text{O}(\text{OH})$], which reduces the activity of the active material by oxidation [84][86].

6.5 Catalyst Deactivation

One of the significant problems related to the operation of heterogeneous catalysis is the catalyst loss of activity with time-on-stream, i.e. "deactivation". This process is both chemical and physical nature and coincides with the primary reaction. Deactivation is inevitable, but it can be slowed or prevented, and some of its consequences can be avoided. Deactivation can occur by several different mechanisms, both chemical and physical. These are commonly divided into four classes, namely poisoning, coking or fouling, sintering, and phase transformation. Other mechanisms of deactivation include masking and loss of the active elements via volatilization, erosion, and attrition. In the following, a brief description of the various deactivation mechanisms will be reported [85][87].

6.6 Catalyst Characterization

In this study, it is necessary to characterize the catalysts used in the catalytic cracking, to determine the effect of the catalyst characteristics of the product yield and distribution, how the catalyst works, the decay activity of the catalyst, and the nature and number of active sites. Instrumental methods are used to characterize the changes that occur in the catalyst during the steam reforming process. These changes are then related to desirable or undesirable changes in the selectivity and activity of the catalyst. Consequently, analytical information concerning both the fresh catalyst and the operating catalyst is essential to the refiner/user as well as to the manufacturer and researcher. Various instrumental methods of analysis are divided into three somewhat arbitrary groups. The techniques within each group tend to provide similar or complementary information, make use of same instrumentation, and involve identical sample preparation techniques [86][88][88]. The three groups are diffractive analysis (XRD), surface area analysis (BET) and thermal analyses (TPD, TGA, TPR). Song *et al.* indicated that the performance difference of $\gamma\text{-Al}_2\text{O}_3$ -, ZrO_2 -, and CeO_2 -supported cobalt catalysts in the ethanol steam reforming could be attributed to the variation of surface acidic and basic properties [87][89].

6.7 Catalyst Preparation

Most catalyst preparations include a combination of selected, or even all these processes although, the preparation techniques fluctuate from one catalyst to another significantly. To categorize the catalysts regarding the current method, three general sorts can be presented. These are impregnated catalysts, mixed-agglomerated catalysts, and bulk catalysts and supports are. Bulk catalysts are mostly included in inactive materials. Combinations to methanol, Silica alumina for hydrocarbon cracking, iron-molybdate for methanol oxidation, Zn-Cr oxide catalyst for the conversion of CO-H, can be significant, and the supports are organized by related processes such as aluminas, silicas, silica aluminas. Generally, by impregnation with the active phase from provided supports, impregnated catalysts are attained. By blending the active materials with a support precursor or crushed support and agglomerating the mixture of the catalysts from the last category of mixed-agglomerated can attain. Several supported metal and oxide catalysts are organized by the substitution of impregnation, calcination, drying, activation and zeolite catalysis which are held by crystallization, precipitation of gel, ion exchange, washing and drying [88][90].

The rising of melted aqueous precursors on oxide support is usually accomplished by the impregnation technique. This term means a process whereby the capacity of the solution, including the precursor of the active component of the catalyst is communicated with solid support. If the ability of the solution either equals or is less than the pore capacity of the support, the method is stated as primary moisture [89][91].

The impregnation technique contains three points: (1) jointing the catalyst support with the impregnating solution in a special time, (2) taking off the imbibed liquid drying necessary support and, (3) activating the catalyst via reduction, calcination or other action. In terms of the overall volume of solution, overflow of the solution and frequent use of solution are two actions of contacting the catalyst support with the impregnating solution. In the first one, the support immersed into an extra amount of solution for the time required for complete impregnation which is located on a screen; after that the solid is drained and dried. The arrangement of the batch solution will alter that process, and the release of residue can create mud which makes it hard to operate the solution. In the second one, a more precise control is attained by this mechanism, impregnation to incipient moisture or dry impregnation. The support is communicated with a solution of suitable concentration, corresponding in the amount to the overall

recognized pore capacity or less. The weakness is the less pronounced of the forerunners [90][92].

7 Experimental Design: Full Factorial Design

During plant operation or the study of chemical reactors, it is crucial to maintain persistence and sound process performance. Equally important is the determination of the optimum performance of the chemical process. To achieve these objectives, it is essential to study the factors that can affect the process and obtain the suitable combination of levels that either maximize the process output or minimize the undesired products from the process. Although the one-variable-at-a-time method can be used for such purposes, the requirement of much resources and time makes it less favorable when dealing with reactions affected by many factors. Regarding previous works; growing the space-time or extending the contact time by increasing the amount of the catalyst can increase the activity of the catalyst [91, 92][93, 94]. However, the catalytic performance also depends on the kind of catalyst or the technique of catalyst preparation[91][93]. To solve this problem, a statistically sound method in the design of experiment (DOE) has been created, which minimizes the time and resources needed in obtaining sufficient experimental data for subsequent analysis. By utilizing suitable software, proper DOE can be used to identify the factors that affect a particular process output (known as a response), followed for optimization, where the optimal settings of the identified factors are determined. The choice of factors and the choice of levels for each element are crucial aspects of the design of any factorial experiment. They will be dictated by subject matter knowledge and constraints of time or cost on the analysis [93][95].

8 Reaction Pathway

8.1 Mechanisms in Steam Reforming and Polymer cracking reactions

With the intention of explaining the formation of the product, as well as the effects of catalysts in steam reforming and catalytic cracking of polymers, several mechanisms were postulated by a number of researchers.

Bio-oil, in particular, has an oxygen content within the 10– 40 wt% range or even as high as 50 wt% and

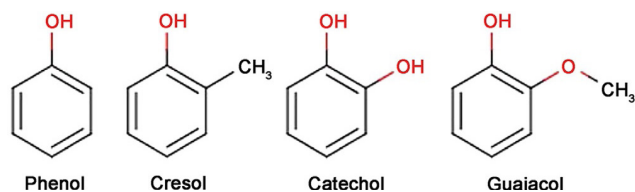


Figure 10: Structures of example phenolic compounds.

water content of 15 to 30 % [94][96]. One solution to these oxygen-related problems is to perform deoxygenation with a heterogeneous catalyst similar to how petroleum oil undergoes desulfurization and denitrification by a hydrotreatment process. In this process, the main objective is to effectively remove oxygen in the form of CO_2 , CO , or H_2O [95][97].

The use of H_2 is typically a significant requirement for the deoxygenation of vegetable oils and bio-oil. However, there is a desire to reduce H_2 consumption and use systems that are either H_2 -modest (low H_2 pressures/flow rates) or which use an inert atmosphere (no H_2) [96][98][98]. The reason for this is because of the cost associated with the use of H_2 and the fact that the majority of the world's H_2 production comes from fossil-fuel reforming. Ideally, biofuels, which are supposed to be considered sustainable and renewable, should not be heavily dependent on non-renewable sources [95][97].

Apart from bio-fuel, most phenolic compounds that are present are either alkyl-substituted phenols, such as cresol, or methoxy-substituted phenols, such as guaiacol (see Figure 10 for examples of phenolic compounds). Relative to fatty acids, phenolic compounds are considered to be more challenging to deoxygenate because of the aromatic structure. A significant challenge for developing deoxygenation process for phenolic compounds in the development of catalysts that can perform deoxygenation without saturating the aromatic rings to minimize the consumption of H_2 (see Figure 11) [97][99].

8.2 General deoxygenation reaction pathways

There are two overall reaction pathways that may be followed for the deoxygenation of phenolic compounds. The first reaction route involves the complete saturation of the aromatic ring, followed by cleavage of the C-O bond likely through dehydration to generate a C=C bond that is to be hydrogenated again [97][99]. This exothermic reaction pathway is often referred to as the “hydrogenation (HYD) route”. The second reaction route is known as the direct deoxygenation (DDO) route and involves a hydrogenolysis

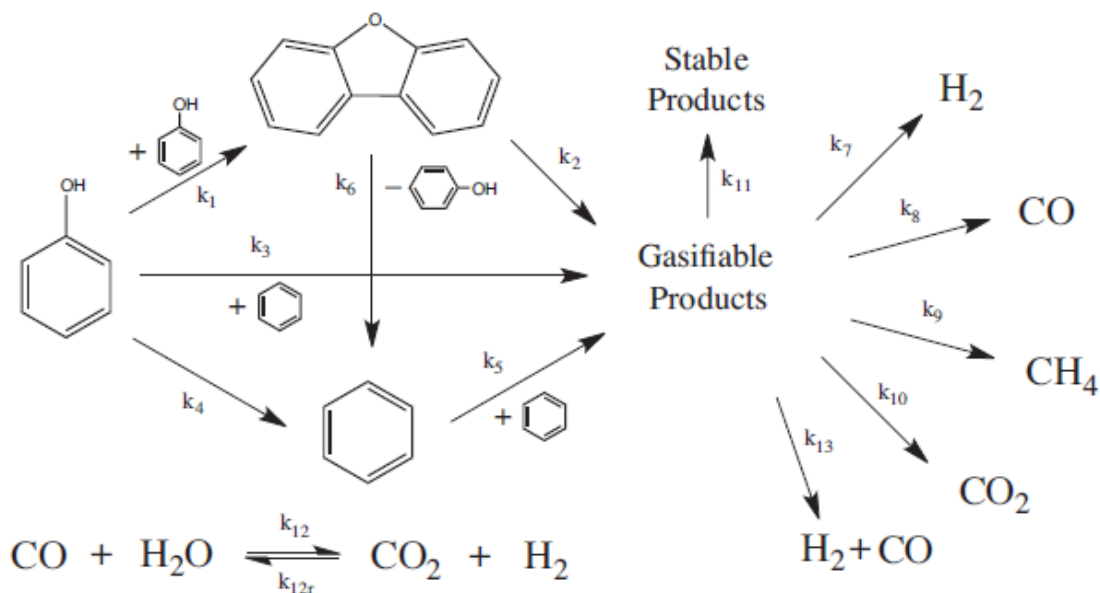


Figure 11: Phenol supercritical water gasification reaction network.

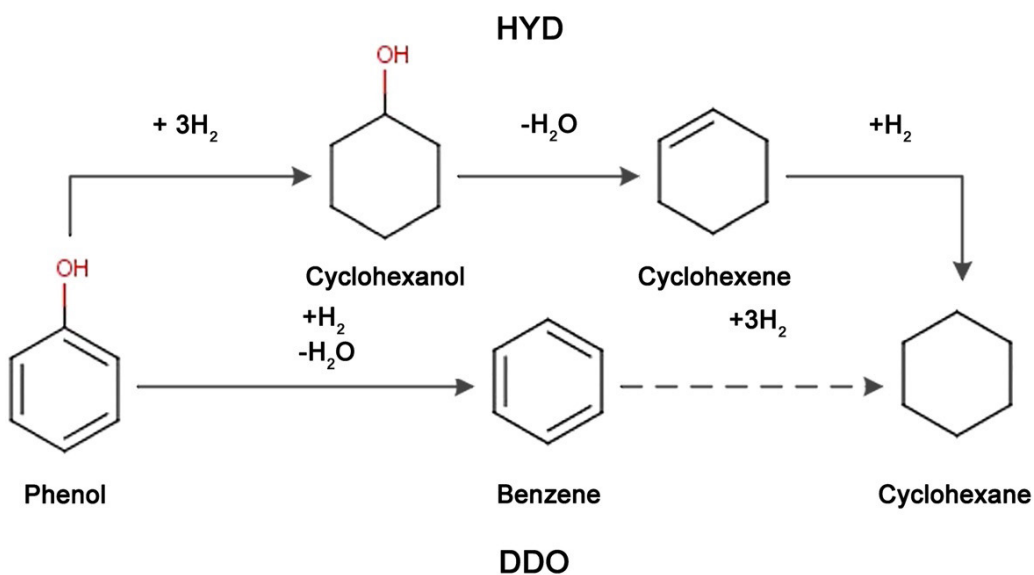


Figure 12: DDO and HYD reaction pathways for the conversion of phenol.

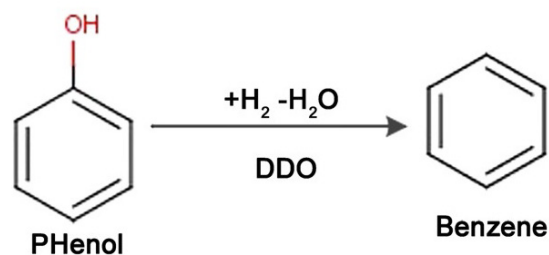


Figure 13: General conversion scheme of guaiacol [95][97][97].

reaction to break the C-O bond selectively while keeping the aromatic structure (see figure 12) [97][99].

8.3 Deoxygenation of substituted phenolic compounds

A hydrogenolysis reaction could break the C-O bond either at the site of the aromatic ring to produce methanol [i.e., demethoxylation (DMO)] or at the methyl group

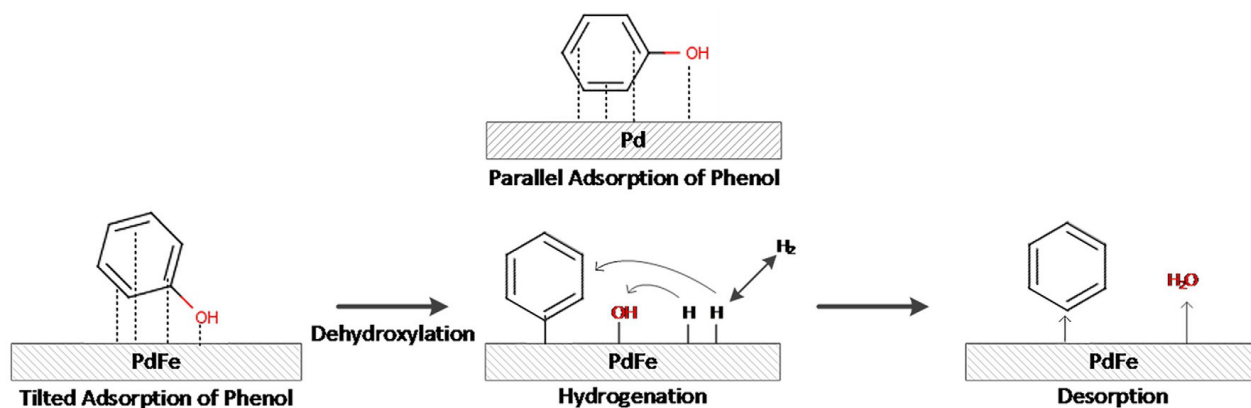


Figure 14: Adsorption of phenol on Pd compared to the adsorption and dehydroxylation of phenol on PdFe [95, 101].

to produce methane [i.e., demethylation (DME)] while leaving a hydroxy group that may undergo subsequent removal from the aromatic ring (see figure 13) [98][100].

Within the past three years, many researchers have focused on the combination of active metals such as Pt, Pd, and Ni with other metals that are typically less active for deoxygenation such as Co, Cu, Fe, and Sn [99] [101]. The consensus is that the addition of the secondary metals alters the catalyst selectivity from promoting HYD reaction routes to promoting DDO reaction routes.

Hensley et al. [100][102] propose a catalytic mechanism for the DDO on PdFe. Through DFT calculations, the most likely catalytic mechanism is dehydroxylation. In contrast to Nie et al., [25a] who propose that adsorption occurs on the Fe atom vertically, Hensley et al. [44c] suggest that phenolic compounds are more stably adsorbed onto the surface more horizontally with weak bonds to the aromatic ring. With phenol as a model compound, the tilted/parallel adsorption mechanism facilitates the direct removal of the hydroxy group to produce an adsorbed phenyl group. [44c] Benzene and water are then produced upon subsequent hydrogenation and desorption (see figure 14).

9 Summary

This paper reviewed hydrogen production from renewable sources. Among the renewable sources of hydrogen production, phenol which was generated as a pyrolysis product was found to be one of the most promising feeds for hydrogen production from the steam reforming process. From the review, catalytic pyrolysis, the reforming of polymer and dissolution of plastic waste in the solvent such as phenol was studied and understood. In line with such development, there is a need to study catalytic reforming of dissolved polymer to produce hydrogen; this

process is advantageous to the polymer recycling industry compared to other process designs. Several challenges have to be resolved regarding such a process, including the selection of an appropriate solvent for the polymer, which is PET in this research. From broad literature surveys and analysis, it can be seen that Ni and Pt are promising to achieve a high hydrogen production level from the bio-oil derivative component with low coke formation. It is also necessary to investigate the effects of different catalysts, and reaction parameters on the polymer conversion, liquid yield, and hydrogen production. Additionally, there is a need to determine the underlying mechanism related to the catalytic reforming of PET-phenol. These issues were addressed in this research using the PET model.

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