ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

A Review of Microwave-Induced Plasma for Production of High Value Products from Waste Glycerol.

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ABSTRACT

The rapid expansion of biodiesel plants dramatically leads to the oversupply of its by-product. Waste glycerol is a low-value by-product of biodiesel production, which are now facing sustainability threats. Developing new industrial uses for glycerol is essential to defray the cost and sustainability of biodiesel industry. Considerable efforts have been devoted to finding applications for converting crude glycerol into marketable valuable chemicals and polymers. However, current state of conversion technologies are still major hurdles with respect to its commercial applications. Therefore, new utilization technologies for glycerol must be develop to reduce the amount of glycerol waste. In the recent years, microwave technology has attracted considerable attention as effective method for significantly reducing reaction time, improving the yields and selectivity of target products. Limited information is available concerning the characteristics of the microwave plasma of waste materials. Due to the unique non-equilibrium characteristics, non-thermal plasma (NTP) could promote a variety of chemical reactions; however, its application in a dehydration process remained blank. Hence, this review strives extensively towards addressing the application of microwave-assisted plasma technology to the as a way of cost-effective and operationally feasible processes to directly utilize crude glycerol from biodiesel production. The present review will focus on production polymer liquid product derived by incorporating of microwave irradiation assisted plasma method. This review concludes that microwave-assisted glycerol conversion technology is a promising option as an alternative method to conventional glycerol conversion technology.

Keywords: Biodiesel; Glycerol; Polymers; Microwave irradiation; Polymerization; Non-thermal plasma

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INTRODUCTION

Global population is predicted to exceed 9 billion by 2050, and the demand for energy dependence on fossil fuels has ongoing increased significantly during the last few decades, with exponentially increase in emission of greenhouse gas CO_2. More than 32.1 metric gigatonnes of carbon emission in the form of CO_2 was emitted globally into the atmosphere in 2016[1].Therefore, in the last decade extensive efforts have been devoted to develop nonconventional energy source such as solar, nuclear, and biofuel, which can replace the dependency of the fossil fuel. In this regard, attention has been paid to biofuel, where renewable biomass-related raw material is converted to valuable chemicals and fuels. Global biodiesel production and consumption is forecast to rise by 14% from 2016 to 2020, driven by the fulfilment of current biofuel policies in the United States, and European Union countries. Although biofuel seem to be a renewable and environmentally benign alternative to fossil fuels, their sustainability is a major concern [2]. One of the concerns is glycerol, the main by-product during biodiesel production through transesterification of vegetable oils and animal fats. For every 10 kg of biodiesel produced, about 1 kg of a crude glycerol by-product is formed[3]. Although glycerol has many uses in various industries, but its surplus is intensely increasing and therefore new applications need to be developed by converting them into valuable chemicals, which could replace petroleum derivatives.It is estimated that global biodiesel production will increase to 37.9 billion litres in 2020 from 33.2 billion litres in 2016, during which almost 3.79 billion litres of crude glycerol would be added to the market [4].Thus, it is vital to convert crude glycerol into higher-value products in order to enhance the economic sustainability of the biodiesel industry and reduce environmental impacts of the crude waste disposal.

Glycerol is a compound with the molecular formula $C_3H_8O_3$; its scientific name is 1,2,3-propanetriol, is one of the most versatile and valuable organic compounds. It is virtually nontoxic and easily biodegradable. It is a useful in production of many pharmaceutical, personal care and food products, to name a few. Traditionally, glycerol was produced through saponification of triglycerides or produced synthetically from propylene, by various routes. Due to the excessive amount of crude glycerol generated as by-product of biodiesel production, the current crude glycerol has become a financial and environmental liability of the biodiesel industry. The resulting glycerol by-product is of low value as it typically contains an estimated 50% impurities such as methanol, water, inorganic salts (catalyst residue), free fatty acids, unreacted mono- di- and triglycerides, methyl esters, and a variety of other organic materials in varying quantities depending on the biodiesel process. Its disposal is also difficult as the methanol content of the glycerol renders its hazardous waste[5].Traditionally, crude glycerol has been used as animal feed or low-grade burning fuel, limiting the commercial value of the feedstock and compromising on the sustainability of the biodiesel production. One route for processing crude glycerol is to produce pure glycerol via refining processes. Further treatments to improve the glycerol by-product quality generally involve neutralization and/or removal of the excess methanol, the catalyst and soap using a vacuum flash process. Depending on the type of separation process used, the final glycerol purity of about 80-95% can be achieved. Purification of the crude glycerol and the conversion into various value added products has been reviewed previously[6,7]. However, these extensive purification process requirements to meet the high purity of glycerol is expensive and economically unfeasible. Despite these advances, the projected production volume of crude glycerol over the next 5 years will largely exceed the present commercial demand for purified glycerol. Consequently, purifying the waste glycerol and selling it as a commodity for traditional applications such as pharmaceuticals, cosmetics and the food industry, is not a practical option for the biodiesel industry. It was reported that the cost of biodiesel production could be reduced by 25% if value of crude glycerol is increased by finding new ways to utilize crude glycerol without the complicated purificationprocess [8].The other alternative route is the direct utilization of crude glycerol into value added products-which can be achieved via either biological or chemical pathways.Over the last few years, exploitation of crude glycerol direct usage has been a very popular topic among researchers. From the technical standpoint, the multifunctional structure and properties of glycerol, provides many opportunities for it to be to modify by several different reaction pathways.

Considerable research has been conducted to develop both chemical and biological processes for the value-added products conversion of crude glycerol. There are a number of articles that have reviewed conversion of crude glycerol to value added products[9,6,10,11,7,12]. Some examples of glycerol-derived products are butanol, 1,3-propanediol, 2,3-butanediol, citric acid, lipid, poly (hydroxyalkanoates), acrolein, monoglycerides, maleated glycerides, polyglycerol, polyols, and bio-oils. These chemicals and polymers have extensive applications as main ingredient in detergents, polymeric materials, pharmaceutical and fine chemicals. However, most of these conversion methods involved a very long reaction time, complicated experiment procedures, pre-treatment of crude glycerol, catalyst sensitivity to the contaminants, and deactivation of the enzymatic pathway caused by glycerol impurities. To justify the direct use of crude glycerol in the production of industrial chemicals, its economic advantage must be substantiated with acceptable end-products yield in a feasible process. Thus, new more sufficiently efficient technologies are needed. Recently, microwave processing (MW) has attracted attention since it satisfies many requirements of green chemistry. Microwave-assisted chemical reactions are now well-established practices, which is able to enhance or influence the outcome of chemical reactions, leading to accelerated and selectivity of the ensuing products.

The review looks at the previous work related to the common path for the usage of crude glycerol namely via the microbial fermentation and the chemical catalytic transformation. A brief overview of these two processes are presented to give a perspective on the utilization of crude glycerol and in particular to highlight the advantages and disadvantages and technical difficulties of both these biological and chemical processes. A relatively new approach for conversion of waste into useful products is the non-thermal plasma technology. Non-thermal plasma has been used as an efficient tool for the removal of atmospheric pollutants, such as volatile organic compounds (VOCs) from ambient air and nitrogen oxides in the flue gas and engine exhaust. Common VOCs, such as benzene, xylene, toluene, formaldehyde, formic acid, trichloroethylene, and dichloromethane, have been studied in the past with the non-thermal plasma technology [13].The microwave-induced plasma is an emerging technology among the non-thermal plasma area and may be used to convert crude glycerol to value added products. This technology will be able to overcoming some of the drawbacks in the current biological and catalytic chemical processes.Microwave-induced plasma is still in developmental stage, and will need greater research activity for it to reach technological maturity. In the near future, the potential conversion of renewable resources into valuable commodity chemicals and polymers using this technology can facilitate greater usage of non-petroleum based raw materials.

UTILIZATION OF BIODIESEL DERIVED WASTE GLYCEROL FOR VALUE ADDED PRODUCT

Glycerol has a large number of applications in varied fields; however, the current market cannot accommodate this large volume of crude glycerol coming from biodiesel production, which needs further costly purification steps. For these commercial applications, the quality of glycerol must be improved until it has an acceptable purity (>98%) [11]. Driven by the motif to search for alternative and sustainable ways of utilizing crude glycerol, many researchers are looking at the production of valuable finish products or intermediate feedstock for the production of new classes of renewable important platform chemicals and polymers. Generally, biomass can be transformed into many useful forms by thermochemical and biochemical conversion. In thermochemical conversion pathways, heat and chemical catalysts are used for the production of chemicals from biomass, while biochemical conversion pathways use biological organisms and biological catalysts for transforming biomass into value-added products [14].The subsequent sub-sections will give a summary of the various potential routes for utilization of crude glycerol the biological and chemical processes.

Crude Glycerol Utilization in Microbial Fermentation

Glycerol, like many other small, uncharged molecules, can be transported through cytoplasmic membrane in different microorganisms, such transport occurs through passive diffusion [15].The production of industrially useful products from crude glycerol is an important issue, as it may be responsible for the price of biodiesel. In most cases, glycerol can be metabolised both oxidatively and reductively through dehydrogenase or dehydratase by a large group of microorganisms to produce high compound. The efficiency of these syntheses depends mainly on the type of glycerol and the microorganisms used. The anaerobic production was focused largely on species within the family of *Enterobacteriaceae,* with particular interest in *Klebsiella* and *Citrobacter*, and members of the genera *Enterobacter*, *Clostridium*, *Lactobacillus* and *Bacillus*[16-19]Table1 shows the microbial transformation of crude glycerol by various microorganism into high-value products. The anaerobic production of these compounds by bacteria has been well reviewed in a number of publications [20,19,9]. The potential for bio-product from waste glycerol is great; however, the industrial recovery of these bio-products is a major issue. Downstream processing is expensive, especially for products that are in low concentrations. In those cases, the bio-products need to have a high value; therefore, the process can recuperate the capital and production costs.

Table 1: Chemicals produced at high yield and/or high productivity by microbial fermentation of glycerol.

Products	Application	Microorganisms	Yield (g/g)	Productivity (g/l/h)	Overall Process Drawbacks	References
1,3-Propanediol	Application in Solvents, adhesives, detergents, resins, and cosmetics. Synthesis of the polyester polytrimethylene terephthalate (PTT), which has application in fibres, textiles, and carpets.	*C. beijerinckii DSM 791*	0.55	0.99	• The recovery and purification of products from complex fermentation broth represents a true bottleneck in the development of a commercially viable bioprocess. • No efficient separation method of products is available for cutting the cost of the conventional separation method, as the separation step requires a substantial energy input. • The major problems with glycerol-fermenting bacteria are the accumulation of undesired by-products, which limited the yield and productivity of the desire product in	[21-28] [15,27,29-41]
		L. brevis N1E9.3.3	0.89	0.78		
		C. pasteurianum DSM 525	nd	0.14		
		S. blattae ATCC 33430	0.45	1.19		
		Mixed cultures (Clostridiaceae, Enterobacteriaceae)	0.52–0.64	nd*		
Butanol	Applied as an industrial intermediate for production of various compounds used in polymer technology such as butyl acetate (solvent in the production of lacquers, polystyrene or phenolic resins), dibutyl sebacate (plasticizer for polyvinyl chloride, ethyl cellulose, nitrile rubber or neoprene), dibutyl phthalate (plasticizer for polyvinyl chloride), 2-butoxyethanol (substrate in the production of acrylic resins or asphalt modifiers). It is also used in the production of nitrocellulose, urea-formaldehyde or melamine-formaldehyde resins.	*Clostridium pasteurianum*	0.35	nd		
Lactic acid	Production of biodegradable polymers and nontoxic esters. It serves as a starting commodity for a wide range of chemicals such as acrylic acid, poly lactic acid, ethyl lactate, and 2,3-Pentanedione production.	*K. pneumonia*	0.82	142.1		
		E. faecalis QU11	0.99	55.3		
		E. coli B0013-070	0.72	14.5		
		P. acidipropionici CGMCC 12230	0.56	0.20		
Propanoic acid	applications as an ingredient in thermoplastics, ant-arthritic drugs,	*Engineered P. acidipropionici Strain*	0.66	nd		

	inhibitory activity against molds, antifungal agents in food and feed, perfumes, artificial derived flavours, solvents, herbicides, cellulose plastics and in production of vitamin E.				pure culture fermentation. • One of the primary issues when using crude glycerol for bioconversions is acquiring microbial hosts which are able to tolerate batch-to-batch variations and the impurities which are found in the crude glycerol . • The presence of contaminants in crude glycerol acting as inhibitory agents, causing microbial growth inhibition, lengthening fermentation time, reduce the activity enzyme biocatalysts and lowering yield and productivity. • Many of the bacteria under investigation are considered	[42-46] [39,20,47-52,15,17] [53,54,39,55] [56,15,57,15,58] [59-62] [62-64] [64,65,9,66,66]
		Propionibacterium acidipropionici	0.475	0.108		
		P. acidipropionici DSM 4900	0.74	0.29		
2,3-Butanediol	Used as a flavouring agent in food products when converted to diacetyl. It can be converted to 1,3-butadiene, for production of synthetic rubber, antifreeze agents, solvents, plastics, liquid fuel additives, polyurethanes for drugs and cosmetic products.	*B. amyloliquefaciens B10-127*	0.38	0.45		
		Klebsiella oxytoca M1	0.44	0.84		
		K. oxytoca	0.14	nd		
Succinic acid	used as a substrate for special chemicals like adipic acid, 1,4-butanediol, tetrahydrofuran, N-methyl pyrrolidinone, succinate salts, gamma-butyolactone polyurethane, food and beverages, resins, coatings and pigments, plasticizers, pharmacy, de-icer solutions, solvents and lubricants, personal care and polymers production.	*Engineered E. coli*	0.69	4.0		
		Y. lipolytica Y-3314	0.45	nd		
Dihydroxyacetone	Applications in cosmetic, food and pharmaceutical industry. Synthesis of fine chemicals such as 1,2-propylene glycerol Biodegradable polymers, nutrient supplement in neural development, and visual acuity and in avoiding cardiac disorder.	*Gluconobacterfrate urii* (CGMCC5397)	90.5%	2.69		
		Gluconobacter frateurii CGMCC 5397	0.89	7.96		
		Gluconobacter oxydans NL71	nd	9.41		
Polyhydroxybutyrate	Used for polyester production, production of medical elements for	*Cupriavidus necator*	50%	1.1		

	internal sutures, and for packaging materials.	*Cupriavidus necator*	nd	0.92	pathogens, require high nutrient medium that increase production costs, need of strict sterilization and anaerobic growth conditions, and tolerate only low-levels of crude glycerol. • Genetic engineering is an interesting option to improve the production of bio-based products from waste glycerol. However, the cost of manipulating and maintaining these microorganisms needs to be considered. • The inhibition of product due to high amount of concentration of the substrates (glycerol), which limits the initial concentration of glycerol. • Microbial cell immobilization	[59-61] [61-,62,9,63,63]
Citric acid	It used as preservative in food and beverages as well as in chemical synthesis, medical, metallurgy and textile industries, chelating agent and as an additive in surfactants and detergents.	*Y. lipolytica*	0.77	0.85		
		Y. lipolytica IMUFRJ 50682	0.42	0.08		
Mannitol	Application in production of medical tablets, mainly for osmotherapy, sweeteners for diabetics, ingredients of chewing gums, adulterant or cutting agent for heroin or cocaine, and polyesters.	C. magnoliae	0.51	0.53		
		Y. lipolytica LFMB 19	0.23	nd		
Oxalic acid	Used mainly in dyeing processes, bleaching agent for pulpwood, baking powder or chelating agent. Application in miticide used by beekeepers, cleaning agent for iron and manganese deposits or used in conductive polymers chemistry.	*A. niger*	0.62	nd		
Erythritol	Used as food additive, and for polyesters production.	*Y. lipolytica Wratislavia K1*	0.56	1.0		
Arabitol	Applications such as in natural sweeteners, caries reducers, sugar substitutes for diabetic patients, and production of polyesters and polymers.	*D. hansenii SBP-1*	0.50	0.12		
		D. hansenii SBP-1	0.6	0.35		
Glyceric acid	Used in the chemical and pharmaceutical industries as a building block and for the production of polymers and surfactants.	*G. frateurii NBRC103465*	0.76	0.81		
		A. tropicalis NBRC16470	0.46	0.71		

Lipid	Represent a valuable alternative feed-stock for biodiesel production.	*Rhodotorula toruloides*	nd	0.083	techniques are other option to even further increases in production yield. The major problem with whole cell immobilisation is the limitation of diffusion of substrate and products through the cell wall.	
		Candida freyschussi	nd	0.43		

Conversion of Glycerol by Chemical Catalytic Process

Crude oil provides the principal source of carbon for the whole of the chemical industry, to fabricate products ranging from plastics to pharmaceuticals. The development of bio-based polymers to replace or reduce the use of polymers from petrochemicals continues to exhibit strong progress. The environmental pollution and waste management issues from bio-resistant synthetic plastics have become increasingly concerning in recent decades. Fossil fuel resources are not sustainable and the significant amount of CO_2 emission from fossil fuel usage is increasing steadily, which may bring about irreversible damage to the environment and climate. The role of polymers in commercial products continues to increase with several hundred millions of metric tons being produced each year, with polyethylene being the largest of global polymer production. Another common polymer that is produced in large quantity from petroleum resource is polyester; a polymer that is cheap and versatile, and for that reason, has become ubiquitous in various applications. However, the environmental impacts of polyester are also significant. More than 70 billion barrels of oil are used to make polyester each year. It is not biodegradable, hence will persist in the ecosystem even as it eventually breaks apart. Stringent environmental regulations have prompted the use of chemicals derived from renewable resources. The development of biodegradable polymers offers an alternative solution. Bio-based polymers have been developed and applied in many fields including packaging, agriculture, and sanitation. Synthetic polymers intended for use in biomedical applications require the additional criteria of biocompatibility and sometimes biodegradability included within the design parameters. However, biocompatibility is usually a built-in characteristic, related to the composition of the (monomer), and is not easily attained by converting it from non-biocompatible raw materials. From a chemical synthesis perspective, glycerol possesses a high chemical diversity and opportunities for selective chemical reactivity and manipulation.

Glycerol is a simple polyol containing two primary and one secondary hydroxyl groups with a prostereogeniccenter at the C2 position. Consequently, glycerol can undergo a large number of chemical transformations such as oxidation, dehydration, hydrogenolysis, and esterification to produce an array of value-added platform molecule building blocks for both small molecule chemical synthesis and polymer synthesis [67-71]. The catalytic conversion of glycerol to value added chemical products have been well documented. A detailed account on the catalytic reactivity of different kind of catalyst in oxidation, dehydration, acetylation, etherification, esterification, acetalization, ammoxidation, and enzymatic process of glycerol conversion was reviewed recently [72]. Many studies on aliphatic polyesters derived from the polycondensation reaction of dicarboxylic acids and diols have been reported [73].

Polymers of glycerol and diacids have garnered considerable interest for the development of bioresorbable materials [74]. The development of new markets for glycerol would also have a significant impact on biodiesel production viability. Generally, efforts to synthesize aliphatic polyesters have focused on other alcohols with little emphasis given to glycerol. Thus, there is a need to explore the use of glycerol, for the synthesis of polyesters. Glycerol can be polymerised; however, most strategies used to make polyglycerols do not use glycerol as the primary propagating unit because the condensation of glycerol is nonselective and requires high processing temperatures [75].

In light of the glycerol glut, the value-added chemical derivatives of glycerol, has attracted great attention in recent years. Crude glycerol is a cost-competitive carbon source (0.04–0.11 USD per kg in the USA, 2011) in comparison to pure glycerol [76]. When crude glycerol isused as a feedstock for the conversion reaction, the impurities would cause operating problems such as deactivating the catalyst. Hence, most of results revealed that the presence of crude glycerol impurities delays the reaction process, leading to lower glycerol conversion, and altered the surface of the catalyst support; which make the catalyst component leached into the reaction mixture [77,78]. Nevertheless, MONG and sulfur compounds caused the most damage on catalytic performance and should thus be eliminated before a reaction occurs. Ashes and methanol must also be removed to prevent the formation of undesirable by-products.In most of the related studies, it is still difficult to obtain good selectivity in the desired products at high glycerol conversion due to the wide hydroxylic functionalization of the triol glycerol molecule of similar reactivity, and owing to unknown reaction conditions or the lack of optimal catalysts. Besides that, the catalyst conversion process has some apparent shortcomings including separation/recovery of the catalyst from the product stream and the use of expensive/toxic solvents in the reaction, which raises environmental and economic concerns for these processes. Furthermore, these catalysts tend to be unstable under the reaction conditions and exhibit decreased activity over time. The deactivation of the catalysts could be due to poisoning, coking, fouling, sintering, or leaching of the metal(s). Nevertheless, significant challenges still need to be addressed in terms of developing chemical platforms under mild processing conditions, design of stable and active catalysts, and essentially different processing techniques for glycerol. Therefore, many researcher are intensively studying catalytic routes that can by-pass isolation and purification steps of crude glycerol. This review describes the recent developments published in this research field.

FUNDAMENTALS OF PLASMA TECHNOLOGY

Plasma which is a fourth state of matter, is formed by ionization of gaseous matter. A Plasma is defined as a fully ionized gas containing a mixture of free electrons, ions, photons, along with atoms in excited state. Plasma is electrically neutral, i.e., electron density is equal to that of positive ions [79]. Plasma can occur naturally or be produced artificially. Solar corona, the solar wind, lightening and the Aurora Borealis are forms of natural plasma. Although omnipresent in the universe and representing nearly 99% of the matter (solar corona, solar wind, earth's ionosphere), the natural presence of plasma on earth is rare (e.g., lightning, aurora borealis) [79]. The plasma can be easily generated artificiallythrough the injection of a sufficient amount of energy to cause gas excitation. In general,plasma is classified into two types: thermal and non-thermal plasma. Their differences are based on the generation mechanism of the plasma. The multi-component plasma system is able to exhibit multiple temperatures. Based on the energy distribution among different components, plasma is normally classified into two types, thermal plasma (TP) and non-thermal plasma (NTP). If the electron temperature (T_e),is much higher than the ion temperature (T_i) and neutral gas species temperature T_g, the plasma iscalled as low temperature plasma or non-thermal plasma. Generally the temperature of this plasma is between 300-1000K. The existence of various types of plasma particles with various degrees of freedoms makes the non-thermal plasma to be thermodynamically in a non-equilibrium state[80]. If all the species are at high temperature such as between 4000 K and 2000 K, the plasma is called as high temperature plasma or thermal plasma. Thermal plasma is typically hot (can be up to 10^6–10^8 K) and the temperatures of different particles are equal due to the quasi-equilibrium in plasma [79,81].The formation of TP requires high power densities, e.g. from 100 W cm^{-3} to 10 kW cm^{-3}[79]. This type of plasma has found wide application in industry including: materials processing, plasma cutting, spray coating, vapour deposition, solid waste treatment, welding and powder disinfection [82].

In non-thermal plasma (NTP), electrons have very high temperatures on the order of 10^4-10^5 K, but the overall gas temperature can remain as low as room temperature [83]. The highly energized electrons (energy lies between 1 and 10 eV) fill the system, and collide with other particles in the system. Because of the large mass difference between electrons and the other particles (molecules, ions, etc.), the collisions are inelastic. The energetic electrons transform kinetic energy into potential energy of the excited species by energizing the atoms and molecules. The energy transfer by electrons is very efficient, and more than 90% of the kinetic energy can be transferred. The energy transferred from electrons to these particles retains potential energy instead of kinetic energy. Therefore, instead of wasting energy for increasing the gas temperature (kinetic movement of the gas particles), the energy is more efficiently and specifically utilized in chemical processes, such as ionization and bond dissociation [79]. A broad range of reactive species can be generated by non-thermal plasma. When the NTP electrons collide with neutral gas molecules, the latter undergo reactions including excitation, ionization and dissociation, and hence free radicals, ions, photons and excited molecules areproduced.NTP features high energy efficiency; the discharge power can be controlled efficiently and selectively. NTP allows the design of unique reaction systems which cannot be realized in conventional chemical reaction at ambient temperature[83].NTP can excite most chemical species, including those that cannot be excited in conventional chemistry or even in photochemistry; NTP can efficiently increase the internal energy of the reactants and facilitate them to overcome the reaction barrier [84]. During collision, the highly energetic electrons can transfer energy efficiently to the reactants for their bond dissociation, ionization, recombination, and so on. High electron temperature, but low overall gas temperature, determines the unusual chemistry in non-thermal plasmas. High energy efficiency, high specific productivity, and high selectivity can be achieved in plasma for a variety of chemical processes [84,13].

To generate non-thermal plasma (NTP), the electron temperature is kept higher than that of ion in gaseous condition at atmospheric pressure. On the other hand, for thermal plasma, the electron temperature is kept in equilibrium with that of the ion. A disadvantage of thermal plasma is that the operating temperature must be between a hundred and at thousand degrees higher than ambient temperature, leading to high-energy loss [79]. This method however, suffers from high temperature, high cost, high heating losses, and lack of sufficient control, problems which hinder commercial application. As such, non-thermal plasma has attracted attention over the last decade due to advantages such as low cost, low temperature, low heating loss, higher removal efficiency, and smaller volume. The recent trends focuses on developing new plasma sources, which operate at atmospheric pressure (low pressure plasmas must be contained in costly airtight enclosures making them highly expensive and time consuming). The economic and operational advantages of operating at 1 atm have led to the development of a variety of atmospheric plasma sources for several scientific and industrial applications. Various methods are available to produce stable NTP at ambient temperature and atmospheric pressure. NTP may be obtained artificially by a diversity of electrical discharges such as DC glow discharge, radio frequency discharge, dielectric barrier discharge, atmospheric pressure discharge, microwave discharge and pulsed power discharge. A wide variation of discharge in the form of corona, spark or arc can be formed in gas or liquid medium using pulsed power with different kinds of reactor configuration; all with important technological wide applications [82,85]. The different methods of non-thermal plasma generation with their constructional and technical views for different sectors have been well reviewed previously [82,86-88].The most common method of non-thermal plasma source generation for technological and technical application can be generated using a variety of methods, producing different non-thermal plasma sources as highlighted in Figure 1.

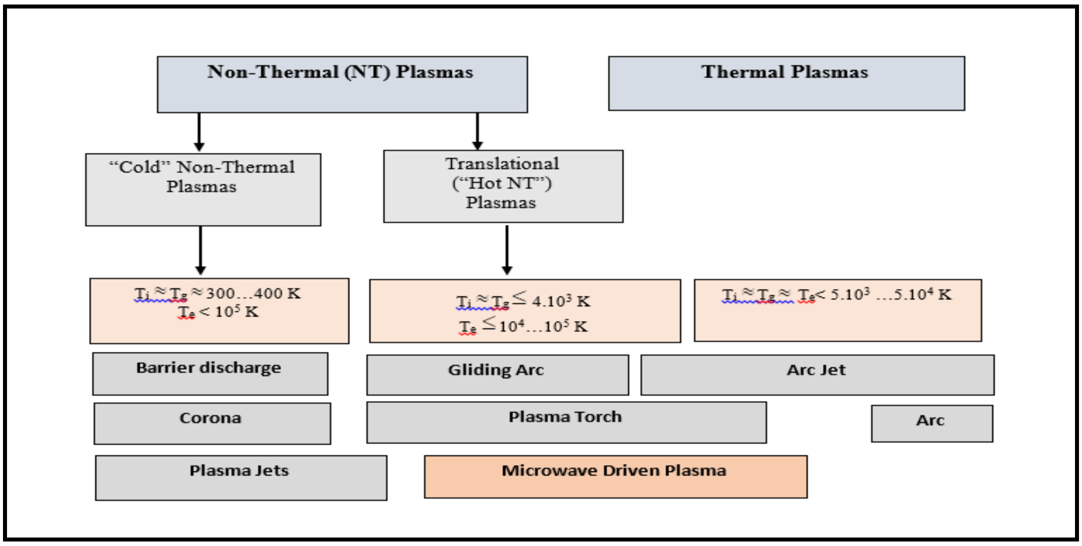


Figure 1: Division of different types of plasmas by the temperature of plasma species.

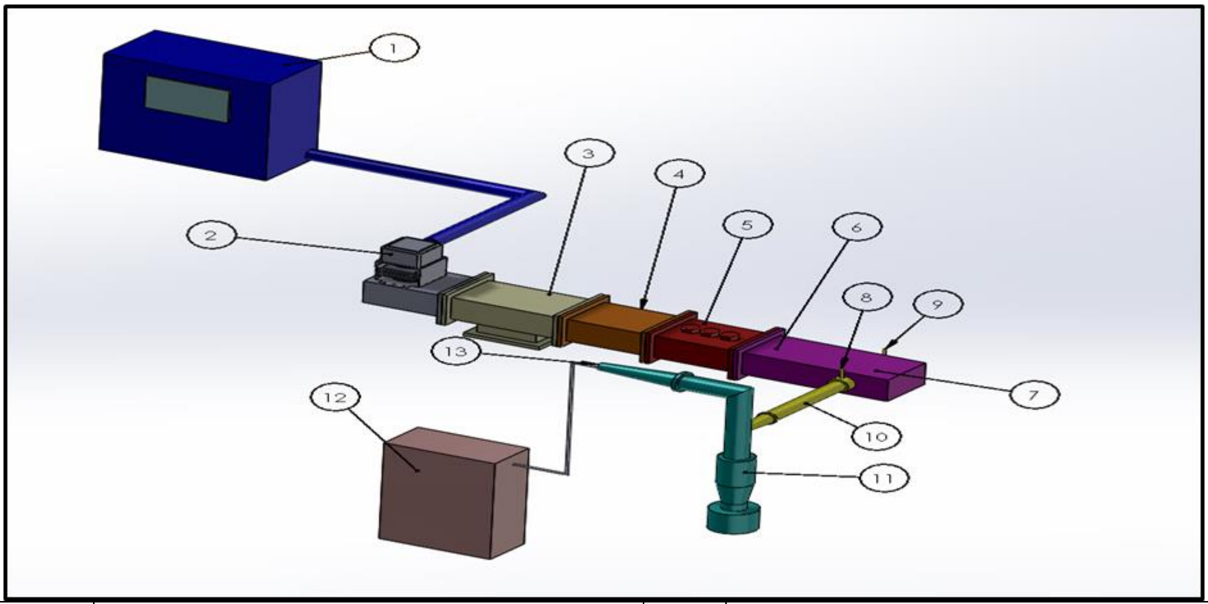
Non Thermal Plasma Applications

High electron temperature, but low overall gas temperature, determines the unusual chemistry of non-thermal plasmas. In NTP, only the motion of electrons is accelerated by an electric field and they capture high kinetic energies. Only highenergy electrons (e*) are present in NTP because the electric field dies away before the motion of the molecules and ions is accelerated. NTP allows the design of unique reaction systems which cannot be realized in conventional chemical reaction media because the high energies of e* are acquired by maintaining the gas at ambient temperature.In non-thermal plasmas, the highly energetic electron plays the most important role in plasma chemical reactions. The high-energy electrons temperature is typically about 10^4-10^5 K, which is high enough to break down bonds of most gas molecules. As a result, there is subsequently production of significant number of energetic and chemically reactive species (e.g., free radicals, excited atoms, ions, and molecules) for the initiation and propagation of chemical reactions [89,90-92].High energy efficiency, high specific productivity, and high selectivity can be achieved in plasma for a variety of chemical processes [83,84,13,93,94].Non-thermal plasma promotes many reactions that are not thermodynamically favourable under normal conditions. In addition, by using different plasma sources or operating gases, the plasma properties can be modified for different application situation.Non-thermal plasma promotes many reactions that are not thermodynamically favourable under normal conditions. In addition, by using different plasma sources or operating gases, the plasma properties can be modified for different application situation. Due to the unique characteristics of non-thermal plasma, it has been widely used in many areas. Among the usage of non-thermal plasma reported are; ozone generation, polymer processing [95-97], removal of air contaminants such as SO_2, NOx, VOC [98-100] and sterilization and disinfection of contaminated surfaces [101,102]. In addition to that there have been reports on usage of non-thermal plasma for surface modification, chemical conversion, light generation and as well as in various hydrocarbons decomposition including natural gas, gasoline, heavy oils and bio fuels[68,103].

Non-thermal atmospheric-pressure plasma was found to inactivate very effectively different microorganisms [104-107] and is able to remove biofilms [108-111]. Even multidrug resistant skin and wound pathogens are susceptible to non-thermal atmospheric-pressure plasma [112-113]. Non-thermal Plasma (NTP) technology represents a novel and sustainable disinfection technology because it inactivates microorganisms without the use of hazardous chemicals. NTP was successfully studied for effective microbial inactivation of *Escherichia coli* from fresh produce [114], *Aspergillusparasiticus* and *Penicilliumsp* from seeds of various vegetable, legumes and cereals [115], Erwiniacarotovora in potatoes [116], Listeria monocytogenes from plastic trays, paper cups and aluminum foil [117]. Complete inactivation of various bacteria including the methicillin-resistant *Staphylococcus aureus* (MRSA) has been reported [118]. Recently, also other skin diseases came into focus for treatment with plasma, e.g. Morbus Hailey-Hailey [119], pruritus [120], atopic eczema [121], psoriasis [122].The mechanisms by which plasma exerts its promising wound healing effects are still under investigation. Other than decontamination, plasma technology works in various other phenomena such as effect on seed germination [123] and retarding browning reaction [124].

MICROWAVE INDUCED PLASMA PROCESS

An article published in 1973, describe the attractiveness of microwave plasma in the field of chemistry and spectroscopy. In microwave plasma, higher degrees of ionization and dissociation was achieved in comparison to other types of electrical excitation employed in the non-thermal plasma [125]. In a typical microwave system, a magnetron generates microwave signal and it travels through a so-called waveguide. Microwave meets the plasma forming gas breaking it into ions, electrons and neutral particles. However, the gas temperature is high enough to decompose stable organic molecules. Based on literature review, most of the microwave induced plasma application studies used magnetron operating usually at 2.45 GHz with highest microwave power of 6 kW. Figure 2 shows the general illustration of microwave plasma system setup [126-141].



No.	Equipment Parts definition	No.	Equipment Parts definition
1	Power Supply and Control Panel	8	Coal + Air Inlet
2	2.45 GHz magnetron	9	Swirl Gas Inlet
3	Isolator	10	Stainless Steel Pipe
4	Directional Coupler	11	Cyclone
5	3-Stub Tuner	12	Gas Analyzer
6	Waveguide	13	Syngas Outlet
7	Field Applicator		

Figure 2: Schematic drawing of the experimental microwave plasma based on gasification application system adopted from [131].

The main parts of the microwave plasma sources are the magnetron (microwave generator). Directional coupler, three-stub tuner (optional), and waveguide [126,142]. Isolator acts as a protective barrier to prevent disturbance from any volatile matter or dust to the heat dissipation of magnetron. Circular running water was installed to carry away reflected power as protection on magnetron from overheating. Meanwhile, 3-stub tuner and short circuit plunger act as a manipulating tool for electromagnetic field inside the waveguide that improves the efficiency of microwave plasma generation by minimizing the reflecting power within the waveguide. Tuning characteristics of cylindrical microwave plasma source was studied by using argon, nitrogen and methane as plasma forming gas under atmospheric pressure environment [132]. Microwave generator was equipped with water insulator, WR430 rectangular waveguide, directional coupler with diode sensors, dual channel power meter and gas supplying system. A movable plunger was placed in the cylindrical microwave plasma to optimize the electromagnetic field. The plasma flame ignition was done by inserting a metallic rod to the discharge space with the purpose of increasing the local electric field [132]. Microwave plasma shows some properties that make it particularly interesting and promising in the context of conversion. First of all, in contrary to most plasma methods, microwave plasma is an electrodeless one. Electrodes are the factor that strongly limits the application of plasma due to their erosion [143,144]. The erosion can be a particularly problematic issue in the presence of oxidizers (like oxygen or steam) or particles which are present in the raw syngas. Secondly, plasma technologies may require an advanced and complicated power source that is designed and manufactured specifically for the purpose of plasma set-up [145]. On the other hand, magnetrons used in microwave plasma are the same that are used in other industrial applications, e.g. drying or food processing. They are relatively cheap and have a simple and compact construction similar to the domestic MW ovens [146]. Moreover, they are produced by many companies and their power can vary from few to hundreds of kW, giving a potential for scaling up of the technology. Lastly, but maybe most importantly, in microwave plasma, a great amount of energy is distributed into vibrational excitation [146]. This physical phenomenon is essential in the chemistry of compounds like CO, CO_2, H_2, and N_2, all of which can be present is syngas [79]. It has been proven that MW plasma is an effective method of conversion of light organic compounds [147] and carbon dioxide [148], resulting in a high content of the most valuable products: carbon monoxide and hydrogen. Microwave-induced plasmas (MIPs) are used extensively for surface modification and the vapour deposition of thin films, and have been used for bulk synthesis [149].

Energy Transfer in a Microwave Plasma

The physico-chemical basics, elaborated for plasmas can be applied to microwave plasmas in special. Therefore, the energy *E*, transferred to a charged species of mass *m* in an oscillating electrical field with frequency *f* is proportional to its charge *Q*, and inversely proportional to its mass *m* and the squared frequency *f* and is a measure of the temperature [150]. In addition to ions and free electrons, a microwave plasma consists of neutral gas species, as well as dissociated gas and finally also precursor molecules for the desired chemical reaction. Therefore, collisions between charged (electrons, ions) and uncharged species (molecules, atoms, or particles) influence the energy transfer to the particles. In this case, the collision frequency *z*, which is proportional to the gas pressure *p*, has to be considered additionally [150].

$$\mathrm{E} \propto \frac{Q}{m}\frac{Z}{f^2+Z^2} \tag{6}$$

As the collision frequency increases with increasing gas pressure, the transferred energy is also a function of the gas pressure. Because of the significant temperature differences of the electrons and the ions, respectively neutral species, plasmas generated with microwaves are considered as non-equilibrium plasmas, or as non-thermal plasmas. They are often called “cold plasma”. These low overall temperatures in microwave plasmas are one reason for the reduced tendency of particle agglomeration during particles synthesis.

Figure 3 shows schematically the calculated relation between the collision frequency *z* and transferred energy *E* on an elementary species applying the two common industrial microwave frequencies, 0.915 GHz, and 2.45 GHz, and, additionally, the less common industrial frequency 5.85 GHz, respectively, and the three different regions of collision frequency to microwave frequency relationship. With increasing frequency the transferred energy decreases: in consequence for nanoparticle synthesis in a microwave plasma, a lower microwave frequency leads to higher reaction temperatures. Lower synthesis temperatures can be realized with higher frequencies. Generally, with increasing gas pressure (meaning collision frequency) the transferred energy increases for $z \ll f$, exhibits a maximum at $f = z$, and decreases for $z \gg f$ [151-153].

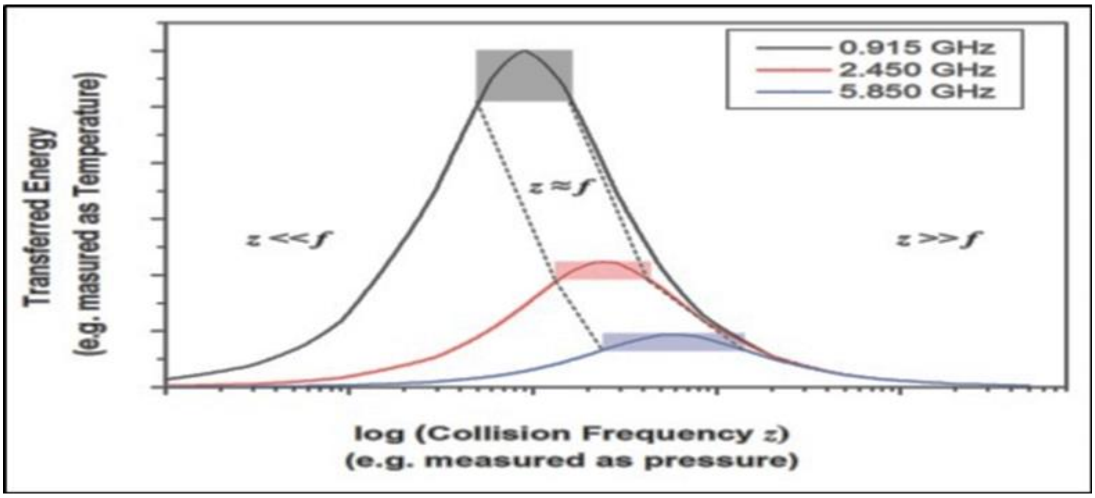


Figure 3: Transferred energy as a function of frequency, calculated using Equation (6) [154]

Most of the theoretical considerations on electrical charging of particles, on coagulation, or selective particle heating have been developed for non-thermal low pressure RF plasmas [155-159].Analogous considerations for microwave plasmas are seldom, but exist [153] showed in model calculations, that charging of particles in a microwave plasma depends on the collision frequency, respectively pressure. Experimental evidence for narrow particle size distribution applying microwave plasma synthesis methods was shown from several groups [160-165]. It is, therefore, most likely that findings for RF plasmas related to particle charging, coagulation, or selective particle heating are transferable to microwave plasmas.

Application of Non-thermal Plasma for Chemical Reactions

The most distinctive characteristic of non-thermal plasma (NTP) is their high chemical efficiency to induce various chemical reactions at atmospheric pressure and room temperature, as no heat is produced, nearly all input energy is converted to energetic electrons. These moderate operating conditions enable a rapid start-up and shutdown of the NTP process at the flick of a switch [87]. The fast electrons produced in a non-thermal plasma can have energies of the order 10 eV or even higher and can therefore trigger many different chemical processes. Besides fast electrons, energetic photons can also play a role in the reactions in a non-thermal plasma. In NTP systems, high-speed electrons are bombarding the bulk gas molecules. This results in production of excited gas molecules such as (N_2^*, O_2^*). The excited molecules lose their excess energy by emitting photons or heat. Ionisation, dissociation, electron attachment and other processes will also occur in the discharge zone [166,167]. This gives formations of unstable reactive species like ions and free radicals [167]. In (NTP), various reactions are initiated by high energy electrons (e*) as stated in Figure 4: excitation (Eq. (1)), dissociation (Eq. (2)), attachment (Eq. (3)), dissociative attachment (Eq. (4)), ionization (Eq. (5)), and dissociative ionization (Eq. (6)). Based on the cross section, Eqs. (5) and (6) are least likely to occur in the normal range of e* energy in NTP [168]. Hence, important historical milestones in the investigation and application of non- thermal plasma chemical reactions are also summarized in Table 2.

$$e^* + AB \rightarrow AB^* + e \qquad (1)$$

$$e^* + AB \rightarrow A + B + e \qquad (2)$$

$$e^* + AB \rightarrow AB^- \qquad (3)$$

$$e^* + AB \rightarrow A^- + B \qquad (4)$$

$$e^* + AB \rightarrow AB^+ + 2e \qquad (5)$$

$$e^* + AB \rightarrow A^+ + B + e \qquad (6)$$

Figure 4: Initial Pathways reaction for high-energy electrons in non-thermal plasma.

Table 2: Applicability of NTP to Specific Chemical Reactions

Plasma Application	Remark
• Synthesis • Fragmentation • Clean-up of gases • Excimer generation	▪ Industrial ozone production, which is used for water or air treatment. ▪ Conversion of methane to higher hydrocarbons. ▪ Applied to reforming methane to syngas. ▪ Converting greenhouse gases into value-added products. ▪ Pollution control ▪ Applied to treat wastewater to control the odor air emissions. ▪ Removal of nitrogen oxides (NO/NO_x) in the flue gas. ▪ Removal of nitrogen oxides in the diesel engine exhaust. ▪ Removal of atmospheric pollutants, such as volatile organic compounds (VOCs). ▪ For light sources

Polymers Production from Crude Glycerol

Acrolein is a uniquely indispensable chemical intermediate with a rising demand in recent years in many industrial applications. Acrolein is the starting material to produce acrylic acid and ester, polyurethane and polyester resin [169].Efforts and improvements in the production of acrolein have been continuously made over several decades. Partial oxidation of propylene catalyzed by multi-component metal catalysts has also been used as a manufacturing method. Several other petroleum-based synthetic routes were used successfully to synthesize acrolein[170]. Acrolein can also be produced via bio-based routes. The acid-catalyzed glycerol dehydration is now categorized as a bio-based route, because glycerol is largely available from biodiesel production, which is originated from renewable biological resources. Recent development of acid-catalyzed dehydration becomes faster, much more selective method with achieved good acrolein yield and great potential use of this method as a substitutive or complementary method to the propylene oxidation route in the future [171]. The solid acid catalyst for gas-phase glycerol dehydration plays the important role in determining whether good acrolein production can be achieved. The major challenge of this method is how to extend catalyst service life to the timescale of months to years. Catalyst deactivation problem was reported in almost every single study on glycerol dehydration to acrolein[172-174]. The negative influence of catalyst deactivation usually reflected in the decrease of glycerol conversion along the reaction time course, which lowered the overall acrolein yield. Catalyst deactivation is caused by coke formation on the catalyst surface, thereby blocking the pores and preventing the glycerol molecules from contacting and interacting with these sites. Glycerol conversion would decrease as the result. Stronger acid sites, or more specifically, strong Brønsted acid sites, are favored by acrolein formation, but they unfortunately also lead to more severe coking and therefore more severe catalyst deactivation [175].

Besides that, liquefaction is another promising alternative methods for the production of polyols. Polyols have been among the major feedstock used to produce polyurethane (PU). PU products, such as foams, coatings, and adhesives, are used daily [176].The liquefaction processes are usually conducted at elevated temperatures (150–250°C) under atmospheric pressure and use polyhydric alcohols. The liquefaction can be either acid- or base-catalyzed, with the former being much more commonly used. During the liquefaction processes, biomass is degraded and decomposed into smaller molecules by polyhydric alcohols via solvolytic reactions. The produced polyols are largely a mixture of different compounds rich in hydroxyl groups and can be used directly to produce various PU products [176]. One of the major drawbacks of these atmospheric liquefaction processes is the use of high volumes of petroleum-derived polyhydric alcohols as the liquefaction solvent, i.e., approximately 100–125 g of solvent are required per 20 g of lignocellulosic biomass to obtain high-quality polyols[177,178].This high volume use of petroleum based solvents considerably increases the production cost of polyols and consequently hinders future commercialization efforts. In the recent years, crude glycerol, a by-product of the biodiesel production process, can be used as an effective liquefaction solvent for the atmospheric liquefaction of lignocellulosic biomass [179,176,180].One of the major challenges of using crude glycerol as a liquefaction solvent is its varying composition. The varying compositions of crude glycerol could cause problems in the consistency of the properties of the produced polyols and PU products. To address these issues, the effects of crude glycerol impurities on properties of polyols and PU foams derived from acid- and base-catalyzed liquefaction processes were evaluated in previous reports [176,180].The base-catalyzed biomass liquefaction process had the advantages of utilizing a wide range of crude glycerol compositions and producing polyols with low acid numbers (<5 mg KOH/g), but suffered from low biomass liquefaction efficiency (i.e., ca.40–65%) and high polyol viscosities [176]. In contrast, the acid-catalyzed biomass liquefaction process exhibited much higher liquefaction efficiency and produced polyols with lower viscosities (<30 Pa s). However, the acid-catalyzed process had the drawback of producing polyols with high acid numbers, which needed further treatments before PU foam production.

Another way of crude glycerol utilization could be its oligomerization and polymerization, also often called etherification, resulting in polyglycerols (PGL). Oligomerization of glycerol resulting in di- and triglycerol has been recently described in comprehensive review of [181]. However in plastics industry, more popular is polyglycerol, highly branched compound, which should be soluble in water and other polar solvents and should be non-volatile at room temperature [182] .Its high functionality and reactivity of hydroxyl groups allow its application in the production of polyurethanes, polyesters, epoxy resins and different copolymers. A number of polyglycerols is commercially available, however majority of them is traditionally produced through anionic polymerization of glycidol in rapid cation exchange equilibrium [183]. Incorporation of crude glycerol could eliminate the use of glycidol, which is considered carcinogenic to humans [184]. Moreover, glycidol is rather expensive compound, whose utilization leads to high cost of the final product, which noticeably limits the wider application of resulting polyglycerols[185]. Polymerization process of glycerol can be performed using different types of catalysts. Acidic catalysis results in high degree of polymerization, but colour properties of the products are affected [186]. Also the selectivity of the reaction is affected and noticeable amount of cyclic polyglycerols is formed [183]. Basic catalysts were found out to be more active than Acidic catalysis, because of their better solubility in the glycerol [187].Even using a preferred catalyst types (based catalyst) the process conditions is still the major obstacles that affect significantly final properties of polyglycerols. Lower reaction temperatures and low pH values lead to the formation of cyclic isomers, while at elevated temperatures side reactions show unfavourable influence on colour and smell of final product [188]. Crude glycerol can be directly transformed to polyglycerols through microwave irradiation in a catalyst-free environment [189].

Hence, obvious disadvantages of most of previous work for applying of one or two different catalysts on different stages of process. These advantages attracted a great attention to catalytic methods in recent years. However, catalytic methods are not flawless. The most fundamental drawbacks are: the catalyst cost, its lifetime, poisoning due to carbon deposit and a resulting efficiency reduction that comes with time [190]. The plasma plays a catalytic role because highly active species such as electrons, ions and radicals which significantly are able to promote the favourable chemical reactions even without catalyst. Those highly active species contain in the plasma are actually thousands of degrees higher than the surrounding temperature, thus promotes the effective rate of chemical reaction and their role is similar to that of catalyst [129,142,140].High reactivity eliminates the need for a catalyst in the systems. Moreover, the plasma high energy density leads to compactness of the system and fast response times can be achieved due to the electrical operation of the system. As a unique heating technology, microwave (MW) has received special attention worldwide. Microwave-assisted conversion have been developed as a promising way that is rapid, energy-efficient, cost-saving, and environmentally friendly to convert this biomass into useful products. MW has been used for chemical synthesis at commercial level and it is also applied to treat the waste materials [191]. Non-thermal microwave drive plasmas operating at atmospheric pressure have been the subject of increased attention during the last decade. It has been shown that high-density microwave plasma provide suitable conditions in order to decompose feedstocks and produce a greener and better quality of products [129].

Microwave-induced plasmas play a significant role in assisted conversion processes. It supplies reactive ions and radicals such as H, OH, and O in a non-equilibrium state, resulting in high performance in the various treatments of materials [192].A study mentioned by [193] have conducted the catalytic reforming of CH_4 and CO_2 to produce H_2 and CO by using plasma induced by microwave. It was found that the conversion efficiency of CH_4 and CO_2 can reach 91.76% and 87.20% respectively, with the selectivity of both H_2 and CO upgraded to approximate 80% by passing through MW discharge area. Experiment by [194] have investigated the conversion of methane to acetylene in microwave-direct current hybrid plasma and found the conversion of methane could reach 84.4% and the yield of acetylene was 63.8%. Additionally, a number of studies have been carried out on the application of microwave discharge plasma to decompose hydrocarbons or alcohols for the production of hydrogen [189-191], to decompose NO [198] and N_2O [199-201], to dissociate CO_2 and H_2O to produce syngas [202]. Furthermore, [192] investigated the gasification of polyethylene (PE) pellets by using atmospheric argon-steam plasma generated by microwave discharge, and found the additional steam to argon plasma promoted the weight decrease of PE and enhanced the production of H_2, CO, CO_2 and CH_4. They confirmed that the steam plasma was effective for the conversion of waste plastic into synthesis gas. As a novel method, MW discharges can physically occur when microwave is exposed on of carbon-based materials leading to a concentrated heat generation and the ionization of the surrounding medium with the formation of high temperature localized hot spots and plasmas [203-205]. The hot spot effect is very helpful for the treatment of those materials that cannot absorb microwave energy efficiently by microwave heating since MW discharges can complement the deficiency in energy absorption, improving the overall heating effect. On the other hand, the plasma effect of MW discharge can also significantly promote the chemical reactions involved. Without any doubts, the broad variety of possible combinations of the hot-spot effect and the plasma effect opens up unique and exciting opportunities for promoting some long and often hard reactions/treatments to achieve a reduction in the processing time and energy as well as an improvement in the product quality. It is believe that the subsequent absorption of microwave energy by plasma provides the high temperature required for cracking of the crude glycerol into atomic carbon to generate a broad range of polymerize products and at the same time to enhance the final yield product. Investigating the appropriate technique for crude glycerol conversion into high value-added products is essential to relieve the environmental pressure and to satisfy some structural requirements in order to compete with petrochemical products.

Production of syngas using plasma gasification from crude glycerol

In the gasification process, biomass is converted into a syngas by the partial oxidation of biomass at high temperatures [206]. Gasification takes place at moderately high temperature and turns solid biomass into combustible gas mixtures (known as synthesis gas or syngas) under limited oxygen supply [207,208]. The main components of this gas are CO, H_2, CO_2, CH_4, H_2O and N_2.The resulting syngas can be burned to produce heat or synthesized to produce liquid transportation fuels [207]. The most conventional used gasifiers are fixed bed gasifiers (FXBG), fluidized bed gasifiers (FBG) and entrained flow gasifiers (EFG). Different gasification agents can be applied, as air, oxygen or steam [209,210]. The use of air as a gasifying agent is most common in industry but yields low heating value gas (4–7 MJ/Nm^3) that is only suitable for heat and power applications. On the other hand, steam and oxygen can increase the heating value of syngas (10–18 MJ/Nm^3) and the H_2/CO ratio. A high H_2/CO ratio is required for producing liquid fuels through Fischer–Tropsch synthesis and also benefits the production of H_2 for use in fuel cells. However, high capital costs and complex system design have hindered the applications of steam and oxygen gasification at a large industrial scale [207,211]. The quality and properties of the product are dependent on the feedstock material, gasifying agent, feedstock dimensions, temperature and pressure inside the reactor, design of reactor and the presence of catalyst and sorbent. Many studies on the utilization of crude glycerol have been conducted in recent years, such as co-gasification with lignocellulosic biomass for enhanced syngas production, among which syngas production, followed by Fischer-Tropsch synthesis to produce green fuels, or followed by water gas shift to produce hydrogen, is of greater interest [212]. Although many studies on syngas production from glycerol have made great advancement, several problems, such as low gas yield, requiring noble metal catalyst and large amount of CO_2 in product gas, have hindered its application [213]. There are different gasification processes available in the literature to produce the syngas. The most important methods and, the most significant studies referring gasification of biomass are compiled in Table 3.

Table 3: Comparison of different types of biomass and gasification process

Process	Feedstocks	Experimental conditions	Outcome of the experimental	References
Dual fluidized bed gasifier	Lignite	Input fuel power: 90 kWth; Particle size: 370 and 510 µm; Steam-to-carbon ratio: 1.3 and 2.1 KgH$_2$O/Kg carbon.	▪ A lower amount of steam and the high catalytic activity of the lignite caused a better performance of the	[214]

			gasification reactor. ▪ The reduction of particle size increases product gas yield in +15.7%.	
	Waste wood; Bark; Plastic residues	Input fuel power: 100 kW; Nitrogen content: 0.05 to 2.70 wt.-%. Temperature: 850°C; Water: 6.1 wt.-% (waste wood); 11.9 wt.-% (Bark)	▪ The DFB gasifier is suitable for the conversion of fuels with higher loads of nitrogen.	[210]
	Empty fruit bunches	Moisture: more than 50 wt.%; Particle size: less than 1.0 mm;	▪ The gasification efficiency decreases as the moisture content increases. ▪ A high content of moisture and oxygen resulted in a low calorific value.	[215]
Fluidized bed gasifier	Pine, maple-oak mixture, and discarded seed corn	Gasifying agent: Oxygen and steam; Temperature: 800°C; Input fuel power: 800 kW	▪ The gasification is most effective for feedstock with low nitrogen and moisture contents.	[207]
Steam gasification	Sugarcane bagasse	Temperature: 800, 900 and 1000°C; Gasifying agent: 8 g/min of steam; Tracer gas: 2.33 g/min of nitrogen; Sample: 15 g of sugarcane bagasse.	▪ The increase in reactor temperature resulted in an increase in energy yield and apparent thermal efficiency. ▪ The enhancement in syngas quality at the 1000°C case resulted in an increase of energy yield.	[216]
	Biomass not specified	Temperature: 800°C to 1200°C.	▪ Higher gasification temperature leads to higher energy efficiencies of product gas and lower energy efficiencies of tar.	[217]
Entrained-flow gasifier	Raw bamboo; Torrefied bamboo; High-volatile bituminous coal	Gasification agent: Oxygen; Sizes of the particles: 44 – 250 µm; fuel temperature: 300 K; Pressure: 2 Mpa.	▪ The carbon conversions of the three fuels are higher than 90%.	[218]
Atmospheric pressure gasifier and the pressurized gasifier.	Forest residue	Moisture: 10 – 20%; Feedstock size: 20 – 80 mm.	▪ In comparison with fuels and chemicals from conventional feedstocks, biomass based ▪ Fuels and chemicals are expensive.	[219]
Fixed bed	Crude glycerol	Temperature: 750–850°C	▪ H_2 concentration	[212]

reactor	with olive kernel	Air ratios of λ = 0.2–0.4	increased from 19 to 33% (v/v) and the tar yield decreased from 19.5 to 2.4 wt% at conditions of T = 850°C and λ=0.4.	
	Pine; Red oak; Horse manure; Cardboard	Temperature: 800°C; Moisture: 12.2 wt.% (Pine), 14.8 wt.% (Red oak) 18.33 wt.% (Horse manure) 12.6 wt.% (Cardboard)	▪ The thermodynamic efficiencies for the gasifier were found in the range of 81.7–84.6%.	[220]
Packed-bed reactor	Mixture of polypropylene and poplar sawdust	Temperature: 400 to 800°C; Particle size: 2 mm (sawdust); 3 mm (polypropylene)	▪ The increase of temperature led to the decrease of the solid residues fraction and an increase in the gas yield. ▪ Optimum temperature: 700°C	[221]

However, conventional gasification process provides significant amounts of “tars” (a complex mixture of higher aromatic hydrocarbons) in the product gas even operated in the 800–1000°C range. A secondary reactor, which utilizes calcined dolomite and/or nickel catalyst, is used to catalytically clean and upgrade the product gas. Ideally, oxygen should be used in these gasification plants; however, oxygen separation unit is cost prohibitive for small-scale plants much longer time to heat up. This limits the gasifiers to the use of air resulting in significant dilution of the product as well as the production of NO_x. Low-cost, efficient oxygen separators are needed for this technology [223]. Plasma gasification is claimed to be a potential alternative technique for solid fuel and waste utilization, that is able to generate power and produce usable by-products as well as clean fuels [135,224,139]. The application of plasma in gasification reactions was claimed to have similar reaction mechanism to that of conventional gasification [225,139]. The main purported benefits of this process are syngas yield with high H_2 and CO content from different types of hydrocarbon feedstock and the conversion efficiencies became nearly 100%. Beside with improved in heat content, low CO_2 yield and low tar content [226]. Thus, it does not require oxygen or it requires only a small amount of oxygen, which is required in the conventional gasification process.With such high temperature, plasma gasification was able to breakdown tars, char, and dioxins [227]. Some researchers worked to decrease the high energy and investment requirements for DC arc plasma by employing microwave plasma, for carbonaceous biomass feedstocks. These investigations were performed at the lab scale ranging from 1–5 kW. [141] examined biomass gasification of glycerol from biodiesel production using a microwave plasma, and obtained an H_2-rich syngas (57% H_2, 35%CO), without any O_2 feed, with a carbon conversion efficiency of 80%. Feeding O_2 decreased the H_2 yield and the calorific content of the gas, with an increase in CO_2 content and carbon conversion.

CONCLUSION

Presented review indicate that incorporation of crude glycerol resulting from biodiesel production into polymer technology is a very promising alternative for conventional production using petrochemical materials. Effective dealing with the surplus of crude glycerol may considerably decrease the cost of manufacturing of different compounds used in plastics production, at the same moment giving more value to crude glycerol as a by-product, which will enhance the economic aspects of biodiesel production. The requirement properties of a product is indeed the most important consideration to evaluate crude glycerol as a raw material. The presence of impurities is acceptable for certain products. Moreover, some methods, allow for simultaneous utilization of other by-products and waste materials, as in the case of liquefaction (utilization of different types of lignocellulose biomass, which is often stored in landfills or subjected to, not quiet economically justifiable, processes as like in the combustion process. The poor conversion of polyols and poly-glycerol derived from crude glycerol can be used to produce rigid or semi-rigid polyurethane foam because of a high maximum specification benchmark for commercial hydroxyl number. The advantages of microwave-induced plasma as mentioned in previously are the ability to operate under atmospheric pressure and ability to elevate to high temperature in short time. Microwave-induced plasma for polymerization of crude glycerol may applicable for polyols and poly-glycerol production. Meanwhile, the effect of microwave power on the other glycerol to be further studied to verify the composition of poly-products.

ACKNOWLEDGEMENTS

The authors would like to thank the University TenagaNasional (UNITEN) for the research facilities. The author Refal gratefully acknowledge the Postdoctoral Research Fellowship from UNITEN BOLD grant. Funding:The E-Sc Research Grant from the Ministry of Science Technology and Innovation Malaysia (e-Sc-03-02-03-SF0287) and UNITEN BOLD Grant (10289176/B/9/2017/5) supported this work.

Authors' contributions: SN and RH conceived and designed the study, and formatted the article. All the authors gathered the data. SN and RH wrote the main manuscript text and performed the discussion. All the authors reviewed the manuscript. SN checked, edited, and approved the manuscript. All the authors read and approved the final manuscript.

Ethics approval and consent to participate: Not applicable.

Consent for publication: Not applicable.

Competing interests: The authors declare that they have no competing interests.

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