RAZA, M., INAYAT, A. and ABU-JDAYIL, B. 2021. Crude glycerol as a potential feedstock for future energy via thermochemical conversion processes: a review. *Sustainability* [online], 13(22), article number 12813. Available from: https://doi.org/10.3390/su132212813

Crude glycerol as a potential feedstock for future energy via thermochemical conversion processes: a review.

RAZA, M., INAYAT, A. and ABU-JDAYIL, B.

2021

sustainability

Review

Crude Glycerol as a Potential Feedstock for Future Energy via Thermochemical Conversion Processes: A Review

Mohsin Raza [1], Abrar Inayat [2] and Basim Abu-Jdayil [1,3,*]

[1] Chemical and Petroleum Engineering Department, College of Engineering, United Arab Emirates University, Al Ain 15551, United Arab Emirates; 201990122@uaeu.ac.ae
[2] Department of Sustainable and Renewable Energy Engineering, University of Sharjah, Sharjah 27272, United Arab Emirates; ainayat@sharjah.ac.ae
[3] National Water and Energy Center, United Arab Emirates University, Al Ain 15551, United Arab Emirates
* Correspondence: babujdayil@uaeu.ac.ae; Tel.: +971-3-7135317; Fax: +971-3-7624262

Abstract: Biodiesel is an emerging substitute for petroleum-based products. It is considered an ecologically safe and sustainable fuel. The high cost of biodiesel production is linearly related to its feedstock. Crude glycerol, which is a by-product of the biodiesel industry, is also a major challenge that must be addressed. A large volume of crude glycerol needs to be disposed of, and this involves processing, dumping, and land requirements. This increases the cost of biodiesel production. One way to decrease the cost of biodiesel production is to utilize its by-product to make valuable products. Crude glycerol can be processed to produce a variety of chemicals and products. The present utilization of crude glycerol is not enough to bring down its surplus availability. Thermochemical conversion processes can utilize crude glycerol as a starting feedstock and convert it into solid, liquid, and gaseous fuels. The utilization of crude glycerol through integrated thermochemical conversion processes could lead to an integrated biorefinery. This review paper highlights the research scope for areas where crude glycerol could be utilized as a feedstock or co-feedstock in thermochemical conversion technology. Various thermochemical conversion processes, namely, gasification, pyrolysis, combustion, catalytic steam reforming, liquefaction, and supercritical water reforming, are discussed and shown to be highly suitable for the use of crude glycerol as an economical feedstock. It is found that the integration of crude glycerol with other thermochemical conversion processes for energy production is a promising option to overcome the challenges related to biodiesel production costs. Hence, this paper provides all the necessary information on the present utilization status of crude glycerol in thermochemical conversion processes, as well as identifying possible research gaps that could be filled by future research studies.

Keywords: crude glycerol; biodiesel; gasification; pyrolysis; liquefaction; steam reforming

Citation: Raza, M.; Inayat, A.; Abu-Jdayil, B. Crude Glycerol as a Potential Feedstock for Future Energy via Thermochemical Conversion Processes: A Review. *Sustainability* **2021**, *13*, 12813. https://doi.org/10.3390/su132212813

Academic Editor: Indra Neel Pulidindi

Received: 13 October 2021
Accepted: 15 November 2021
Published: 19 November 2021

1. Introduction

Global warming and crude oil depletion are two of the greatest challenges of the 21st century [1]. Both these concerns must be effectively addressed by the scientific community by proposing substitutes for fossil fuels in order to maintain a sustainable society [2]. At present, fossil fuels are the dominant source of energy generation, which ultimately leads to the emission of greenhouse gases (GHGs) [3]. The excessive penetration of CO_2 into the atmosphere is causing climate change globally as well as regionally [4]. GHGs also have a lethal effect on human health [5]. The National Oceanic and Atmospheric Administration reported in 2019 that the CO_2 concentration in the atmosphere was 407 ppm [6]. If the CO_2 concentration continues to grow, there will be an average increase of 1.1–6.4 °C in the world's temperature by the end of this century [7]. Renewable sources of energy show great promise in this scenario. Renewable energy sources, such as biomass energy, solar energy, wind energy, and geothermal energy, are green energy resources for energy production [8]. These renewable sources have great importance when there is energy storage to resolve the problem of their intermittency [9]. Both the concerns of environmental protection and energy security can be catered to by exploiting renewable sources of energy [10]. Biomass has great potential in this context, as it is renewable and works on the basis of the carbon fixation process [11]. During its utilization, biomass only releases the amount of CO_2 that it has consumed during the photosynthesis process of its growth [12]. However, briefly, the most commonly used biomass materials for energy generation and for the synthesis of different chemicals are agricultural waste residues as they do not compete with food crops [13]. Worldwide, biomass makes a significant contribution of about 15% of the total renewable energy consumption. This share is approximately 90% in rural areas of developing countries, as biomass is the primary and most easily accessible source of energy [14]. There are three main conversion processes for the transformation of biomass into different products. The selection of the conversion route depends on the required end-product [15]. The three biomass conversion technologies are thermochemical conversion, biological conversion, and chemical conversion [16]. Figure 1 represents an overview of these biomass conversion technologies.

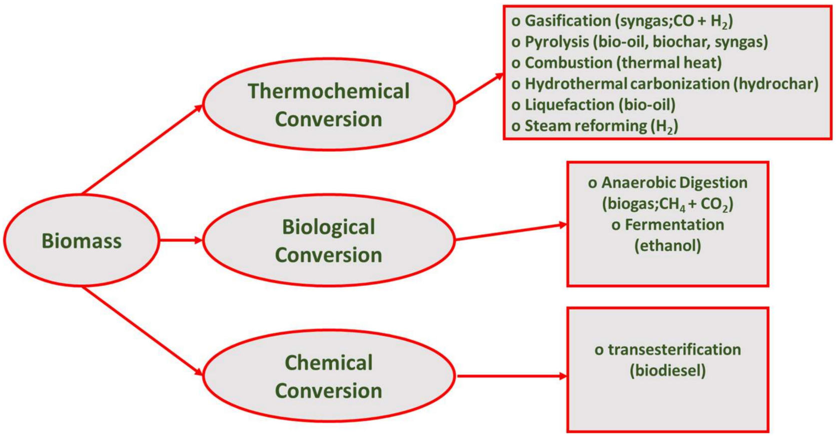

Figure 1. Biomass conversion technologies.

Biodiesel produced by the chemical conversion process of biomass is the best alternative to fossil fuel-derived diesel. It has many advantages over conventional fuels, and its share is continuously expanding in the commercial fuel market [17]. In 2017, a report by the Organization for Economic Co-operation and Development (OECD) stated that the world biodiesel production was around 36 billion liters in the respective year [18]. The biomass feedstock for biodiesel production varies across different regions [19]. For example, palm oil is the dominant biomass material for biodiesel production in Malaysia, whereas soybean oil is dominant in the USA and rapeseed in Europe. With a biodiesel production capacity of 13.5 billion liters, the European Union held the position of the largest producer of biodiesel in the year 2017, followed by the USA with a production capacity of 6.9 billion liters [20]. However, the high production cost of biodiesel hinders its complete commercialization to replace petrodiesel. The cost of the biomass feedstock is the leading parameter that makes up the cost of the biodiesel produced [20,21]. One way to overcome this problem is the utilization of the by-product of the biodiesel production process for various purposes [22]. Glycerin, most commonly known as glycerol, is the by-product of the biodiesel production process [1–3]. Nearly 5 kg of crude glycerol is produced for the production of approximately 46 kg of biodiesel [23–26]. The utilization of this non-toxic material with the potential to be used in versatile applications could lead to declining biodiesel costs [27]. Among the various utilization options, the most lucrative application for glycerol consumption is to use it as a feedstock in thermochemical conversion processes. All the thermochemical conversion processes have strong potential for massive-scale utilization of glycerol as a feedstock material. Before using crude glycerol or any other lignocellulosic biomass in bioenergy production, it can also undergo different processes, among which pretreatment plays an important role in the yield, productivity, and quality of the products [4–6]. The penetration of biofuels into existing energy systems has an important role in the development of smart and clean cities. Therefore, the production of crude glycerol from the biodiesel industry will continue to grow [7,8].

The unique structure of glycerol is responsible for its properties that make it a prominent candidate for numerous applications [28–33]. Glycerol has a hygroscopic and water-soluble nature, which is due to its backbone containing three carbon atoms along with three hydrophilic hydroxyl groups [34]. Without any chemical treatment or purification step, it is called crude glycerol [35]. The purity of crude glycerol varies between 60% and 80%, while commercially synthesized or pure glycerol has 99.5–100% purity. Impurities in crude glycerol are alcohol, inorganic/organic salts, water, heavy metals, monoglycerides, soap, fatty acid methyl esters, free fatty acids, non-glycerol organic matter, ash, and diglyceride traces [35]. The density, pH, viscosity, color, ash content, and water content of crude glycerol and pure glycerol are 1.01–1.20 and 1.30 kg/m^3, 2.0–10.8 and 6.4, 1213 and 930 $mPa \cdot s$, dark brown and colorless, 2.7–5.7% and nil, and 1–28.7% and nil, respectively [36,37]. Pure glycerol is the main feedstock for the production of pharmaceutical products, beverages, surfactants, cosmetics, food additives, lubricants, and many more items. The purification of crude glycerol on both small and large scales is an expensive process. The impurities in crude glycerol make the purification process costly, so the areas where it can be utilized in crude form are of great importance [38].

Many researchers have already reviewed the possible applications of glycerol for its utilization. Leoneti et al. [35] reviewed studies on the utilization of crude glycerol as a raw material for chemical production, hydrogen production, fuel additive production, and development of fuel cells. Vivek et al. [35] reviewed strategies for the development of waste to wealth by transforming crude glycerol into value-added chemicals. Okoye et al. [39,40] reviewed reactor systems that can be used for the synthesis of glycerol carbonate, which is a valuable product made from crude glycerol. Monteiro et al. [41] reviewed patents related to the utilization of crude glycerol between the years 1993 and 2015; the results indicated that the major use of crude glycerol is in synthesizing different chemical products, production of polymer compounds, and the production of biogas. Aqilah et al. [42] reviewed the electrochemical conversion of crude glycerol and the factors that affect the reaction pathways, rate of reactions, product selectivity, and yields. Electrochemically converted glycerol has many uses in the pharmaceutical, cosmetics, food, and polymer industries. Dou et al. [43] and Haron et al. [44] reviewed the potential of crude glycerol as a feedstock for hydrogen production. The price of crude glycerol is continuously dropping on the market as biodiesel production is unceasingly increasing [45].

However, since the abundant quantity of crude glycerol needs to be accommodated in vast applications, it would be helpful to highlight its utilization potential in many other research areas as well. Presenting its utilization needs in different areas will contribute towards its quick exhaustion. Therefore, this work aims to provide a comprehensive review from the renewable perspective with a focus on the utilization of crude glycerol from the biodiesel industry as a feedstock/co-feedstock for thermochemical conversion processes. As per the literature review, there is no review available that focuses on the valorization of crude glycerol with thermochemical conversion processes. The authors believe that this is the most practical and beneficial way of bringing down the processing cost of biodiesel. The objective of this review is, therefore, to present the potential of crude glycerol as a feedstock/co-feedstock for thermochemical conversion processes such as gasification, pyrolysis, combustion, catalytic steam reforming, liquefaction, and supercritical water reforming. The readers will learn about the current status of crude glycerol formation from the biodiesel industry, insights into different thermochemical conversion processes, and schemes through which these integrated conversion processes can be optimized together with bringing down the cost of biodiesel production.

Crude glycerol as a feedstock/co-feedstock is assessed with the following six thermochemical conversion processes:

1. Biomass gasification
2. Biomass pyrolysis
3. Biomass combustion
4. Catalytic steam reforming
5. Liquefaction process
6. Supercritical water reforming

The concept of hybrid conversion processes, in which a by-product of the chemical conversion process is utilized as a feed/co-feed for thermochemical conversion processes, appears to be the most suitable way of utilizing crude glycerol without any purification step. The outcomes and possibilities for future research studies are presented for each hybrid process investigated from the available research studies in the literature.

2. Chemical Conversion of Biomass Material

Transesterification of biomass is the most common conversion process for the production of biodiesel [9–11]. The process has attracted great attention in recent years because a variety of vegetable oils can be converted into products with technically favorable fuel properties [12,13]. Biodiesel is the main product of this imperative chemical conversion process. The viscosity of the vegetable oil is reduced and brought into a range comparable to conventional petrodiesel fuel [46–51]. The most commonly used plant oils are canola, babassu, palm, crambe, sunflower, jatropha, soyabean, caster bean, and oilseed radish [52]. The transesterification process is also known as simply alcoholysis because the vegetable oil is made to react with alcohol [53]. The most frequently used alcohols are ethanol and methanol as these are easily and cheaply available. The process converts the triglycerides into esters in the presence of a catalyst [54]. The most common factors that affect the transesterification process are reaction time, catalyst type, alcohol to oil ratio, and reactants' grade [14–18].

The transesterification process can be classified as either catalytic transesterification or non-catalytic transesterification [55–60]. Catalytic transesterification processes have some limitations. These processes are time-consuming and need a separation process for the mixture of oil, catalyst, alcohol, and saponified impurities in the biodiesel [61]. The supercritical transesterification process requires no catalyst during the conversion process and involves no saponification. However, the supercritical transesterification process is limited due to the requirements of high pressure and temperature, which raise the cost of the biodiesel [62]. Acid-catalyzed transesterification is used when the free fatty acid (FFA) content in the oil is more than 1%. The process decreases the FFA amount and increases the yield of alkyl esters [63]. Base-catalyzed transesterification is used when the FFA is less than 1%. This involves the conversion of triglycerides into alkyl esters and glycerol. The less dense biodiesel is removed from the bottom denser layer of glycerol by the separation process. The separated biodiesel is washed with water. Anhydrous sodium sulfate is used to dry the biodiesel [64]. The generalized equation for the transesterification process can be seen in Figure 2. Furthermore, Figure 3 gives an overview of the acid-catalyzed and base-catalyzed transesterification processes.

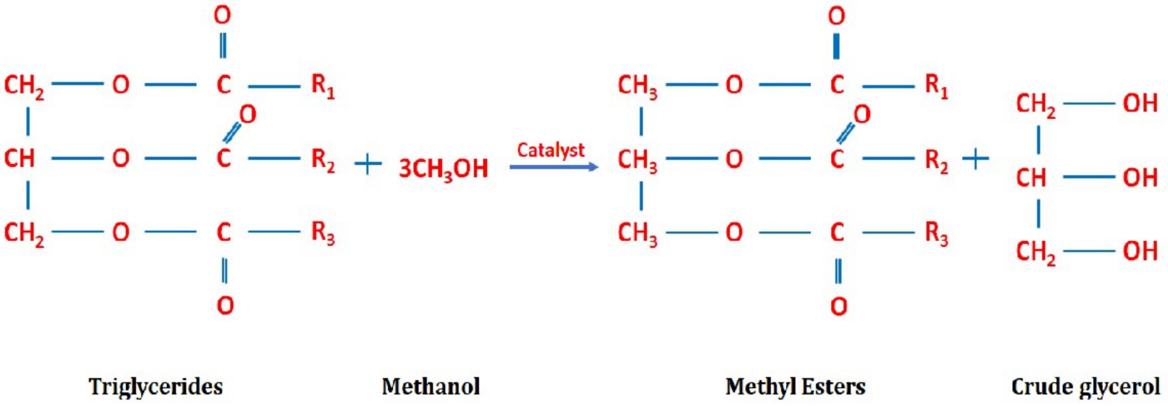

Figure 2. Transesterification reaction for biodiesel production (adapted from [65]).

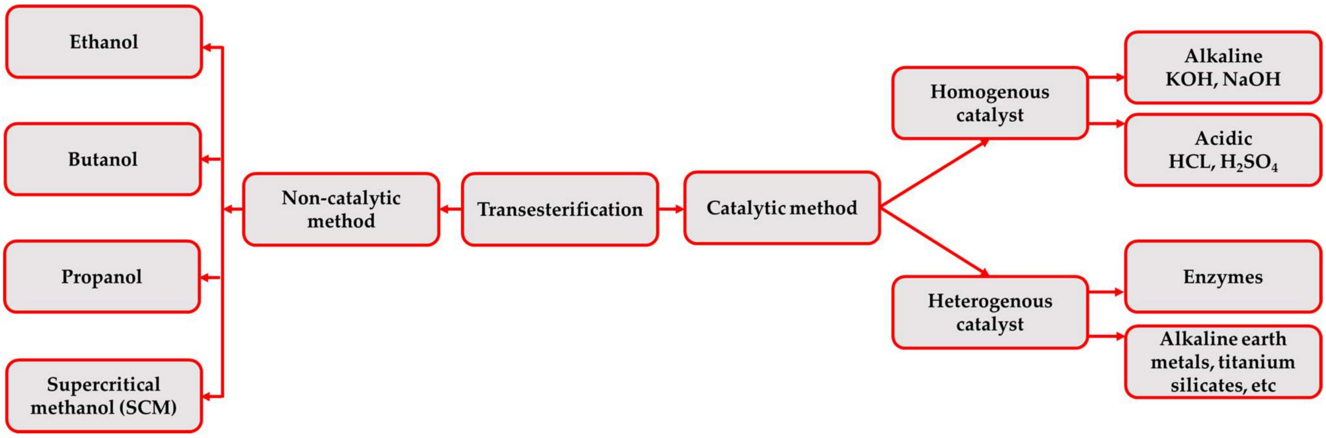

Figure 3. An overview of catalytic and non-catalytic transesterification processes (adapted from [66]).

The following are the advantages of biodiesel when compared with conventional petrodiesel [19,20]:

1. Biodiesel releases reduced emissions such as CO_2, CO, SO_2, PM, and HC compared with petrodiesel.
2. Biodiesel production is easier than fossil-based diesel production.
3. It makes the vehicle accomplish improved efficiency because it has a cetane number of over 100.
4. Biodiesel does not need to be drilled, transported, and refined like petrodiesel.
5. When biodiesel is produced locally, it becomes more economical than petrodiesel.
6. Biodiesel has improved fuel characteristics in terms of sulfur content, flash point, aromatic content, and biodegradability.
7. Higher combustion efficiency and no engine modification required till B20.

In addition to the above-mentioned advantages of biodiesel over petrodiesel, researchers are now also investigating the effects of biodiesel on engine performance and characteristics. Hoang el at. [67–70] evaluated and analyzed the origination and mechanism of deposits formed in the injector of diesel engines running on biodiesel or biodiesel blends. The influence of three main factors, namely, fuel components, temperature, and injector configuration, on the level of formed deposits was analyzed. It was suggested that the oxygen content and incomplete combustion are the leading causes that should be addressed to overcome biodiesel-based deposits and meet the standards of petrodiesel. In another study, Hoang el at. [71] suggested that the same engine performance can be achieved by using different compositions of biodiesel blended with petrodiesel. They found that using rice bran-based biodiesel, a blend containing 20% v/v biodiesel with petrodiesel gave the most efficient techno-economic performance in existing engines while mitigating environmental concerns. Moreover, Hoang el at. [72] also suggested that the issue of corrosiveness of some metal alloys, such as copper-based alloys, aluminum-based alloys, cast iron, carbon steel, and stainless steel, in existing petroleum-based diesel engines due to fueling with biodiesel can be eradicated with different strategies. Higher corrosiveness due to biodiesel as compared to petrodiesel appears to be due to its higher hygroscopicity, higher electrical conductivity, higher polarity, higher solvency, higher oxygen content (promoting microbial growth), and auto-oxidative nature (generating corrosive agents). They concluded that biodiesel can be made fit to use in existing engines by the development of novel alloys coated by layers resistive to biodiesel and doping of biodiesel with corrosion inhibitors. Biodiesel has been emerging as a promising biofuel strategy for reducing toxic emissions and improving engine performance. Computational approaches, such as artificial neural networks (ANNs), could provide a good ability to predict the engine behaviors with an accuracy higher than 95% [73].

Concerning the amount of crude glycerol that is produced during the transesterification process, it is estimated that for every 1 m^3 of biodiesel produced, 0.1 m^3 of glycerol is also produced. The volumetric ratio for biodiesel to crude glycerol production is 10:1 [74]. In 2015, the worldwide biodiesel production was estimated to be 30 million m^3, which means approximately 300,000 m^3 of crude glycerol was produced [47]. As the boom in the biodiesel industry continues, there will be a further increase in the amount of glycerol. In 2011, only 40% of the total 5 million tons of glycerol was utilized and the remaining was all left over [74]. The growing volume of crude glycerol from biodiesel production is a growing concern for the sustainability of this industry because of the high cost associated with the disposal and purification. Crude glycerol is a versatile renewable material used in many industrial and chemical industries [75]. It is mainly used in sweets, cakes, meats, and cheeses as a humectant. It is also used in foods and beverages as a sweetener, solvent, and preservative. This gives color and flavor to soft drinks [41]. The increased availability of biodiesel has boosted the applications of crude glycerol. However, the present utilization of crude glycerol is not capable of absorbing the total production [33]. Therefore, there is interest in highlighting its potential uses in various other fields. In recent years, crude glycerol has emerged as a potential feedstock to be used for thermochemical conversion processes.

Other than the transesterification conversion process, there are also some other processes to produce biodiesel such as pyrolysis, microemulsification, and blending [76]. Pyrolysis, the thermochemical route of biomass conversion, is employed at a temperature above 350–800 °C to get a product distribution of biofuel, biochar, and synthesis gas. The pyrolysis process is simple, pollution-less, and does not require washing or filtering. The disadvantage lies in the need to have expensive equipment and high temperature and pressure. Microemulsification involves mixing oil/fats into alcohol (solvent) and surfactant until the required viscosity is obtained. The most significant advantage of this conversion process is that it is pollutant-free, cheap, and simple in its operation. The limitations of this process, such as moderate viscosity and lower stability, do not allow high-end applications [20]. Blending is just the mixing of vegetable oil with petroleum-diesel at a ratio of 10–40 wt./wt.% and merely using it in the diesel engine without any modification. This process does not demand any technical improvements in the engine. The process can lead to certain limitations with increased vegetable oil in petrodiesel due to higher viscosity, less volatility, and improper atomization [77,78]. The transesterification conversion process produces higher conversion with relatively lower cost, it has mild reaction conditions, the biodiesel properties are closer to petrodiesel, and it is suitable for industrial-scale production. The major disadvantages of this process are that it requires low free fatty acids and water content in the feedstock, and that it involves possible side reactions, extensive separation and purification, and huge wastewater generation [79].

3. Thermochemical Conversion Processes

Thermochemical conversion of biorenewable feedstock leads to the production of various useful chemicals and fuels by the employment of different possible routes. The biomass material can be converted into solid, gaseous, and liquid forms for the subsequent production of thermal heat, electricity, chemicals, and liquid and gaseous fuels. The thermochemical route of biomass conversion includes gasification, combustion, hydrothermal carbonization, and pyrolysis technologies. Each of these conversion processes gives a different type and composition of energy product [21–24]. Therefore, the methodology of the present review paper is to evaluate the possibilities of utilizing crude glycerol in different thermochemical conversion processes. Details of each respective thermochemical conversion process are provided. Then, the previous research studies that involved the utilization of crude glycerol as a feedstock/co-feedstock are presented to draw a conclusion for that thermochemical conversion process. The review paper reveals the current status of crude glycerol's usage in different thermochemical processes and presents guidelines and research gaps for conducting future research studies.

3.1. Biomass Gasification

The biomass gasification process consists in partial oxidation of solid organic feedstock to produce a gaseous phase and a solid phase. The gaseous phase is known as syngas, which has a higher heating value. Syngas can either be used for heat generation (direct burning for thermal heat) or for power generation (electricity production through generators). Syngas can also be converted into biofuels with the application of different catalysts [80–84]. A typical composition of syngas consists of carbon monoxide (CO), hydrogen (H_2), methane (CH_4), and carbon dioxide (CO_2). It also contains small amounts of lighter and heavier hydrocarbons such as ethane, propane, and tars, respectively [85]. Tar is an undesired component in syngas, which condenses at a temperature range of 250–300 °C, and it also lowers the efficiency of the biomass gasification process [86]. The resultant solid phase from biomass gasification is known as char. Char is the unreacted organic fraction and inert material present in the treated biomass feedstock [87]. The gasification of biomass takes place in the presence of a gasification agent. The most commonly used gasifying media are air, O_2, CO_2, and steam. The selection of gasifier carrier depend on the requirements of the type and composition of end-products [88]. The lower heating value (LHV) of syngas varies between 4 and 13 MJ/Nm^3. The LHV of syngas adjusts in relation to the biomass feedstock type, gasification technology adopted, and operational conditions [89]. The biomass gasification process consists of four separate distinctive stages. The main gasification reactions take place in the endothermic stages, and the required heat is internally generated by the exothermic stage involving the partial oxidation of biomass feedstock, reaching a temperature as high as 850–1200 °C [90]. The main stages of biomass gasification and the main reactions are shown in Figure 4. Biomass gasification uses a variety of biomass feedstocks, and in recent times, this technology has been extensively used for the gasification or co-gasification of crude glycerol to produce syngas. A summary of the studies available in the literature for gasification of crude glycerol is presented in Table 1. It can be seen from the available research studies that gasification technology using crude glycerol is a viable option to obtain a comparative syngas yield when lignocellulosic feedstock is utilized. Moreover, in some studies, the utilization of crude glycerol as a co-feedstock improved the syngas yield. Gasification using crude glycerol is therefore undoubtedly a promising option; however, more research is required in using it with different reactor configurations. Most research is done using fixed bed reactors, which are mainly suitable for laboratory-scale investigations due to the convenient ash-handling system. Crude glycerol gasification/co-gasification using fluidized bed technology, such as bubbling fluidized and air-circulating beds, could be a good option for future research studies.

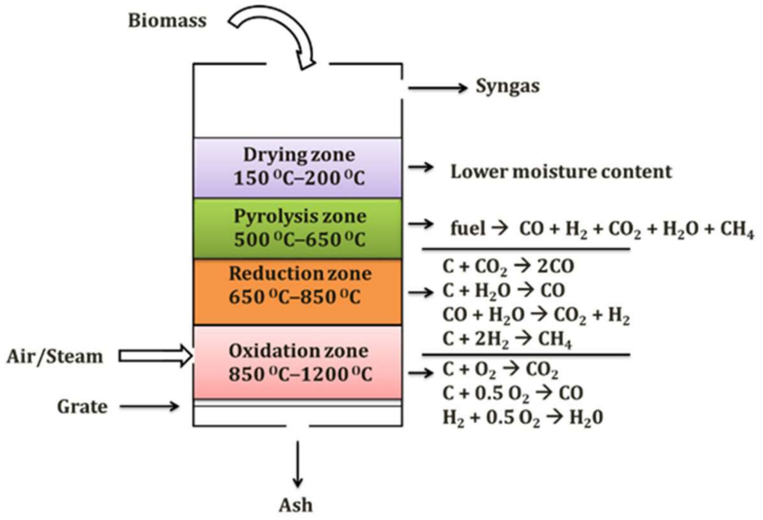

Figure 4. Biomass gasification chemistry.

Table 1. Crude glycerol as a feedstock in various gasification conversion processes.

Gasification Technology	Biomass Feed	Oxidizing Agent	Operating Conditions	Remarks	Refs.
Downdraft fixed bed reactor	Crude glycerol 85.5% (v/v)	Steam	750–1000 °C	There was no technical difference between the crude glycerol and technical glycerol dry gas yield. HHV_g 15 and 14 MJ/m^3 for technical and crude glycerol, respectively.	[91]
Downdraft fixed bed reactor	Crude glycerol/fat co-gasification (glycerol = 40.7 wt.%, water = 57.6 wt.%)	Steam	800–950 °C	The analysis of the dry gas revealed that crude glycerol/fat co-gasification is a technically feasible option. Dry gas yield of 1.4 m^3/kg. HHV of 15.8 MJ/m^3.	[92]
Fixed bed reactor	Crude glycerol/olive kernel co-gasification	Air	750–850 °C, air/biomass ratio = 0.2–0.4	A reasonable dry gas yield of 1.2 Nm^3/kg was obtained with a good amount of H_2 (33% v/v) in the gas yield. HHV of 8–10 MJ/m^3.	[93]
Downdraft fixed bed reactor	Crude glycerol/hard wood chips co-gasification	Air	600–700 °C	The addition of crude glycerol with hard wood chips co-gasification up to 20 wt.% increases the combustible gas ratio (CO and CH_4) in the synthesis gas mixture.	[94]
Downdraft fixed bed reactor	Crude glycerol (glycerol wt.% = 77.6, water wt.% = 11, and ashes wt.% = 4.2)	Steam	682–1018 °C, water/glycerol solution 0.7/3.3 wt./wt.	Gasification temperature and water/glycerol ratio influence the composition of syngas. Both the steam reforming efficiency (SRE) and carbon gasification efficiency (CGE) were influenced by these two parameters. LHV was 14.40 MJ/Nm^3.	[95]
Fixed bed reactor	Crude glycerol/water	Steam (indirect contact)	600–900 °C, water/glycerol ratio 6–12 wt./wt.%	Higher gasification temperature enhances the water–gas shift reaction, which favors more H_2 production. H_2 molar fraction of 67.4%, and HHV = 9332.8 KJ/Nm^3.	[96]
Downdraft fixed bed reactor	Crude glycerol	Steam	800 °C, two different packing materials (quartz and silicon carbide)	Crude glycerol was completely converted into gas and char at steam/glycerol ratio of 50:50. The same optimum conditions resulted in the best yield of synthesis gas (91.1 wt.%). Syngas and calorific value were 92 mol% and 13.5 MJ/m^3.	[97]
Entrained flow gasifier	Crude glycerol (glycerol wt.% = 60, and unreacted triglyceride = 20 wt.%)	Air and oxygen	900–1500 °C	The comparison study between air and oxygen blown gasification shows the best results with an optimum value of crude glycerol gasification, and with an excess air ratio of 0.35–0.40. The syngas HHV, carbon conversion, and cold gas efficiency were 2500 $kcal/Nm^3$, 92%, and 65%, respectively.	[98]
Tubular reactor	Crude glycerol/physic nut/palm shell co-gasification	Air and nitrogen	700–900 °C, biomass/glycerol ratio = 70/30, air factor 0.0–0.6	A linear relation was found between temperature range (700–900 °C) and gas yield. The maximum gas LHVs were 3.48 MJ/m^3 and 2.27 MJ/m^3 for glycerol waste mixed with physic nut waste and palm shell waste, respectively.	[99]

Table 1. *Cont.*

Gasification Technology	Biomass Feed	Oxidizing Agent	Operating Conditions	Remarks	Refs.
Fixed bed furnace	Crude glycerol (36.40% C, 8.76% H_2, 0.67 S, and 54.17% O_2)	Steam	700–800 °C	Both olivine and Ni/olivine catalysts showed good performance for producing syngas and with higher conversion of waste material into H_2 and CO. LHV of 4.65 MJ/m^3 for runs with Ni/olivine at 800 °C.	[100]
Stainless steel tubular reactor	Crude glycerol (NaCl, NaOH, methanol, and free fatty acids as impurities)	Steam	Factorial design: T = 804 °C, steam/carbon ratio = 2.2, oxygen/carbon ratio = 0	The crude glycerol hydrogen yield (4.4 mol H_2/mol glycerol) was nearly identical to that obtained from commercially available reagent-grade glycerin. Production of 1.4 mol H_2/mol and 1.4 mol CO/mol of glycerin.	[101]
Fixed bed reactor and autoclave	Crude glycerol	Aqueous phase reforming (APR)	160–280 °C, feed concentration = 5–85 wt.% glycerol	It is found that 230 °C and a feed flow rate of around 0.73/h with a glycerol concentration of 45 wt.% is favorable for maximum H_2 production, which is 67%.	[102]
Fixed bed reactor	Pure glycerol/crude glycerol	Steam	800 °C, liquid hourly space velocity (LHSV) = 0.77/h	The final yield of syngas from the crude glycerol and pure glycerol under steam gasification was 83.3 mol% and 93 mol%, respectively. For crude glycerol-based syngas, the heating value is in the range of 13–13.9 MJ/m^3.	[103]
Microwave gasification (tubular reactor)	Crude glycerol (36.40% C, 8.76% H_2, 0.67 S, and 54.17% O_2)	Steam	500–1400 °C, 110–880 watt, Ni-based catalyst	The optimum conditions for the microwave-assisted gasification of glycerol were 1% Ni/SiC, 600 °C, 330 W. The operating conditions yielded a gas product with a heating value of 9.18 MJ/m^3 and H_2/CO ratio of 1.32.	[104]
Downdraft fixed bed reactor	Crude glycerol	Steam	850–950 °C, Al particles as bed material.	At 950 °C, the gasification system achieved 90% carbon conversion efficiency, 100% H_2 conversion efficiency, and a maximum lower heating value of 14.5 MJ/m^3.	[105]
Microwave plasma gasification	Crude glycerol	Oxygen and steam	2 kW microwave generator	In plasma gasification, it was found that the fuel droplet size, mixing effect, and the retention time inside the plasma flames influence the syngas yield and gasification efficiency. The carbon conversion and cold gas efficiency were improved by up to 4.5% and 7%, respectively.	[106]
Fluidized bed reactor	Crude glycerol	Steam	600–800 °C	Unlike the fixed bed reactor, the fluidized bed reactor eliminates catalyst deactivation. At a certain time in the fluidized bed, the net coke production rate approaches zero. Mole fraction 40–60 mol% under different process conditions.	[107]
Fluidized bed quartz reactor	Crude glycerol	Oxygen	700–800 °C	The ratio of H_2/CO was close to 1. The lower heating value of gas is evaluated as 0.8–4.9 MJ/m^3.	[108]

3.2. Biomass Pyrolysis

The thermal decomposition of biomass feedstock in the absence of oxygen is known as biomass pyrolysis. Pyrolysis converts lignocellulosic biomass into a variety of carbonaceous-rich gaseous, liquid, and solid fuels. Cellulose, hemicellulose, and lignin are the main components in lignocellulosic biomass materials. The temperature range for biomass pyrolysis is 300–500 °C, which is moderately lower than the gasification process [25–29]. The key products from the pyrolysis process are bio-oil, biochar, and synthesis gas [109–114]. Based on temperature and heating rate, pyrolysis technology is further classified as slow pyrolysis, fast pyrolysis, intermediate pyrolysis, and advanced pyrolysis. All of these types have their own different types and composition of products [115]. Table 2 represents an overview of the various biomass pyrolysis technologies and their associated process parameters and products.

Table 2. Summary of different biomass pyrolysis technologies [116].

Pyrolysis Type	Heating Rate (kg/s)	Residence Time (s)	Temperature (°C)	Particle Size (mm)	Products
Slow	<1	300–1800	400	5–50	Char
			600		Gas, oil, char
Fast	500–10^5	0.5–5	500–650	<1	70% oil
					15% char
					15% gas
Flash	>10^5	<1	<650	<0.2	Oil
		<1	>650		Gas
		<0.5	1000		Gas

However, the two most frequently used pyrolysis techniques are slow and fast biomass pyrolysis [117]. Slow pyrolysis of biomass is related to slow heating rate, moderate temperature, and long retention time. Biochar is the main product of slow biomass pyrolysis with a lesser amount of other by-products [118]. The opposite is the case in fast biomass pyrolysis, which occurs at relatively high temperature, higher heating rate, and very short residence time. It produces bio-oil as its main product, which is very good in quality as compared with that produced from the slow biomass pyrolysis process [119]. Solid char from pyrolysis can also be used as a feed in the gasification process [120]. A typical pyrolizer consists of a reactor, cyclone, and condenser. Firstly, the lignocellulosic biomass is fed into the reactor and thermochemical reactions take place to decompose it into different products. The solid products are then separated from the liquid and gaseous products with the application of a cyclone. Finally, the gaseous products are quenched into the condenser to produce bio-oil; hence, bio-oil is separated from the remaining gases. The non-condensable gases are mostly recycled into the main pyrolysis reactor to support fluidization or improve thermal efficiency [121]. Sometimes, catalysts are also used in biomass pyrolysis processes to improve the quality and quantity of product yield [122]. There are numerous types of pyrolysis reactors that can be used for different pyrolysis categories. In slow pyrolysis, the most commonly used reactors are drum, rotary kiln, and auger/screw reactors. In fast pyrolysis of biomass, the most common type of pyrolysis reactor used is a fluidized bed reactor. The fluidized bed reactor can either be a circulating fluidized bed or a bubbling fluidized bed reactor. Other pyrolysis reactors used for fast pyrolysis are rotary cone, entrained flow, and ablative reactors [123]. The many advanced biomass pyrolysis techniques include vacuum pyrolysis of biomass [124], microwave pyrolysis of biomass [125], flash pyrolysis of biomass [126], biomass pyrolysis via plasma technology [127], and biomass pyrolysis via solar energy [128]. Microwave pyrolysis has advantages over conventional heating as it includes homogenous internal heating [129].

Biomass pyrolysis is an established renewable energy technology and has a high positive environmental impact [130]. In the literature, a reasonable amount of research has been conducted using crude glycerol as a feedstock in the pyrolysis process. Crude glycerol has been utilized to obtain solid char, bio-oil, and synthesis gas. An overview of these studies is presented in Table 3. It can be seen that there was an improvement in the bio-oil quality and quantity when co-pyrolysis of different lignocellulosic materials, such as corn straw, olive kernels, corncobs, and sugarcane bagasse, was performed with crude glycerol. It is known that the feedstock composition and heating rate have a great influence on the pyrolysis product distribution. Therefore, future research studies could focus on investigating the synergistic effects of crude glycerol co-pyrolysis with other lignocellulosic materials to identify the reaction mechanisms and kinetics parameters for a suitable reactor configuration and enhanced energy production. In addition, crude glycerol pyrolysis/co-pyrolysis can be performed using advanced pyrolysis technologies to target a specific product distribution and yield.

Table 3. Crude glycerol as a feedstock in various pyrolysis processes.

Pyrolysis Method	**Biomass Feed**	**Glycerol Properties**	**Operating Parameters**	**Remarks**	**Refs.**
Flash pyrolysis	Crude glycerol/lignite	Glycerol = 85.4 wt.%, moisture = 8.4 wt.%, free fatty acids = 0.2 wt.%	300–1000 °C/s, 650–850 °C	Highest H_2 yield (65.44% *v*/*v*) at 850 °C and for a crude glycerol blend of 20 wt.%.	[131]
Slow pyrolysis	Crude glycerol/corn straw	Glycerol = 56.2 wt.%, methanol = 7.3 wt.%, water = 2.4–4.3 wt.%	30 °C/min, 550 °C	With a blend of crude glycerol with corn starch (1:1), the gas yield was increased from 23 wt.% (for pure crude glycerol) to 39 wt.%, with reasonable LHV = 29 MJ/m^3.	[132]
Fast pyrolysis	Crude glycerol/olive kernels	Glycerol = 85.4 wt.%, moisture = 8.4 wt.%	450–800 °C	Crude glycerol with olive kernels at 25 wt.% mixture and at 750 °C gives an 11.65% increase in H_2 concentration in the synthesis gas.	[133]
Microwave pyrolysis	Crude glycerol/olive kernels	-	450–750 °C, 50 °C/s	The highest gas yield (59.53% *w*/*w*) was obtained at T = 500 °C. An increase in gas yield (84.9% *v*/*v*) was achieved as compared to non-microwave pyrolysis (79.1% *v*/*v*).	[134]
Microwave pyrolysis	Crude glycerol	99% glycerol	400–900 °C	Using microwave heating with crude glycerol, a temperature of 800 °C is the most suitable for converting it into a higher amount of pyrolysis gas (81% *v*/*v*).	[135]
Catalytic slow pyrolysis	Crude glycerol/ZSM-5/bentonite	Glycerol = 49 wt.%, water = 2.43 wt.%, free fatty acids = 44.5 wt.%	550 °C, 30 min under He flow	The study successfully demonstrated the use of ZSM-5/bentonite catalyst to produce bio-BTX.	[136]
Slow pyrolysis	Crude glycerol/macroalgae	>99 wt.% glycerol	60–280 °C, 5–10 °C/min	The highest biochar yield (47.28%) was obtained at crude glycerol/macroalgae ratio= 5:1, temperature = 320 °C, and retention time of 50 min.	[137]
Fast pyrolysis	Crude glycerol/corncobs	Analytical reagent, solid to liquid ratios = 5–20%	220–240 °C, 0.5–3 h,	Crude glycerol/corncob pretreatment by a pyrolysis process was carried out, and then the material was subjected to microbial fermentation.	[138]
Microwave pyrolysis	Crude glycerol/sugarcane bagasse	Glycerol purity > 99.7%	60–240 °C, 10 °C/min	Crude glycerol was used for the pretreatment of sugarcane bagasse and then further subjected to a pyrolysis process. The levoglucosan yield increased to 25.2% as compared to crude glycerol (14.4%) and sugarcane bagasse (8.4%).	[139]

3.3. Biomass Combustion

Direct combustion of biomass has been practiced by humans since the invention of fire in the Stone Age [140]. Biomass combustion consists of various homogeneous and heterogeneous reactions. Biomass feedstocks are mainly composed of carbon, hydrogen, and oxygen; therefore, the main products of biomass combustion are carbon dioxide (CO_2) and water (H_2O) [141]. There are various factors that determine the maximum combustion temperature. The flame temperature can exceed 2000 °C, and it depends upon the influence of the following aspects: (i) heating value of the fuel, (ii) moisture content within the fuel, (iii) air/fuel ratio, and iv) furnace design [142]. Three requirements must be fulfilled to initiate the combustion process. These three requirements are fuel, air, and heat (ignition source) [143]. The combustion process becomes self-sustaining when all these are present in an accurate proportion. Air contains 21% oxygen and 79% nitrogen. Therefore, the stoichiometric equation of combustion also considers the amount of N_2 released along with CO_2 and H_2O [144]. The stoichiometric equation of combustion is as follows [145]:

$$\text{Biomass} + \text{Air} \rightarrow CO_2 + H_2O + H_2O\ (_V) + N_2 + \text{Heat} \tag{1}$$

However, some biomass materials contain more traces of elements other than C, O, and H; therefore, in this case, the stoichiometric combustion equation will contain a few more products [146]. Moisture content is vital in combustion process chemistry; if it is excessive, then the spontaneous combustion will require additional fuel [147]. The combustion process is also responsible for numerous pollutants such as hydrocarbons (HC) and nitrous oxide (NO_x). Biomass combustion is mostly carried out to generate thermal heat and mechanical work [148]. Biomass co-combustion with coal is often practiced in process industries for firing steam boilers. The two most important technologies for biomass combustion are biomass in the grate and combustion in the fluidized bed [149].

Since crude glycerol is a by-product of a green process, directly burning glycerol does not add anything to the environment. Using glycerol as a feedstock for industrial fuel has many benefits. Direct combustion of crude glycerol as boiler feed is the simplest method for its utilization. It does not require any purification or processing for its combustion. If this thermal energy is integrated into the biodiesel production facility, it reduces the cost of biodiesel and causes less reliance on fossil-based energy [150]. Crude glycerol has a moderate lower heating value (LHV), which is approximately 16–20 MJ/kg. The difference in LHV depends on the type of raw material used in biodiesel production [151]. The combustion of glycerol is as per the following stoichiometric equation [152]:

$$C_3H_5(OH)_3 + 3.5\ O_2 \rightarrow 3\ CO_2 + 4\ H_2O\ (v) + \text{Heat} \tag{2}$$

Researchers are working on the combustion of glycerol to overcome some of the limitations in its direct utilization. Bohon et al. [153] conducted an experiment on the combustion of crude glycerol. They concluded that crude glycerol combustion as a source of heat and power has the limitations of lower energy density, lower auto-ignition temperature, and high viscosity, which need to be addressed. It was found that crude glycerol's auto-ignition temperature is 370 °C, which is comparably high as compared to kerosene (210 °C) and gasoline (280 °C). Corondo et al. [154] evaluated the combustion performance of crude glycerol used as a boiler feed in the biodiesel industry. The concept of environmental efficiency was evaluated based on CO_2, No_x, and SO_2 emissions. It was found that USP (refined glycerin) has better ecological performance than the methylated and demethylated glycerol samples. Co-combustion of crude glycerol with other biomass materials is also a feasible option. Alnaqbi et al. [155] co-combusted dry tree leaves with crude glycerol. It was found that the combustion gives the best efficiency when dry tree leaves are mixed with 20 wt.% of crude glycerol. In general, this method is not feasible from an environmental perspective. Moreover, due to lower combustor performance prospects, crude glycerol combustion/co-combustion has not been explored in much detail.

3.4. Steam Reforming Process

Steam reforming is one of the most mature technologies. It is the leading technology to produce hydrogen (H_2) from natural gas (CH_4) [156]. Many other feedstocks can also be treated with the steam reforming process such as methanol, liquid petroleum gas, diesel, jet fuel, and naphtha [157]. The steam reforming process is enhanced with catalytic action. Catalytic deactivation is therefore an issue for which most of the research is being undertaken [158]. The products from the steam reforming process are hydrogen (H_2), carbon monoxide (CO), and carbon dioxide (CO_2) [159]. Steam reforming of crude glycerol is a thermochemical conversion process that leads to the conversion of low-cost by-products into hydrogen. The following is the reaction mechanism of glycerol [160]:

$$C_3H_8O_3 + 3H_2O \rightarrow 7H_2 + 3CO_2 \quad \Delta H = 128\ \text{kJ/mol} \tag{3}$$

$$C_3H_8O_3 \rightarrow 4H_2 + 3CO \quad \Delta H = 250\ \text{kJ/mol} \tag{4}$$

$$C + H_2O \rightarrow CO + H_2 \quad \Delta H = 131\ \text{kJ/mol} \tag{5}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H = -41\ \text{kJ/mol} \tag{6}$$

$$C + 2H_2 \rightarrow CH_4 \quad \Delta H = -75\ \text{kJ/mol} \tag{7}$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad \Delta H = -206\ \text{kJ/mol} \tag{8}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad \Delta H = -165\ \text{kJ/mol} \tag{9}$$

$$C + CO_2 \rightarrow 2CO \quad \Delta H = 172\ \text{kJ/mol} \tag{10}$$

In the literature, a considerable amount of research has been performed on catalytic steam reforming of crude glycerol. However, most of the research has been carried out on catalytic steam reforming of pure glycerol, but the results and catalytic activities can be related to research on crude glycerol. Table 4 presents an overview of the technical details of the studies conducted on steam reforming of crude glycerol from the biodiesel industry. Table 5 presents an overview of catalysts that have been employed in steam reforming of pure glycerol. Therefore, the catalysts that are presented in Table 5 have the potential to give favorable results when applied to catalytic steam reforming of crude glycerol. In this process, catalysts play a dominant role in the enhanced yield of combustible gas (H_2 and CO). Here, impurities in the crude glycerol can negatively affect the catalyst performance. The activity and durability of catalysts can be compromised. Therefore, future research could be done on catalyst development. Furthermore, in situ CO_2 sorption in catalytic steam reforming can be integrated to increase the hydrogen yield and drive the reaction mechanism in the forward direction. Moreover, in Table 5, although nickel catalysts are more affordable, noble metals such as Pt, Ru, and Ir are more effective and operational at cooler temperatures [161]. On the other hand, earth-abundant MnO_2 has also been reported as an efficient catalyst [162].

Table 4. An overview of studies on steam reforming of crude glycerol for H_2 production.

Catalyst Type	Crude Glycerol Properties	Operating Parameters	Remarks	Refs.
Ni-based catalyst and in situ CO_2 sorption	70–90 wt.% glycerol, water, and methanol < 15 wt.%	400–700 °C, atm pressure, fixed bed reactor	Steam reforming with in situ CO_2 removal over Ni-based catalyst produced H_2 with nearly 90% purity. Crude glycerol and steam conversions were 100% and 11%, respectively.	[163]
Ni-Cu-Al, Ni-Cu-Mg, Ni-Mg catalysts	-	450–650 °C, atm pressure, fixed bed reactor	Ni-Cu-Al catalyst with 39.7 wt.% gave the best catalytic activity, with conversion of crude glycerol up to 91%. The H_2 selectivity was also highest (92.9%) with this catalyst.	[164]
One-stage sorption enhanced SR with Ni/Co catalyst	Glycerol = 70–90 wt.%, H_2O and CH_3OH < 15%, inorganic salts < 5%	550–600 °C, atm pressure, fixed bed reactor	Using an Ni/Co catalyst, this single-stage sorption enhanced steam reforming (SESR) process gave H_2 with very high purity (99.7 vol.%) and good yield (88%).	[165]
Pt/Al-based catalyst	Glycerol = 33 wt.%, CH_3OH = 23%, H_2O = 3.2%, ash = 3.8%, free fatty acids = 40%	880 °C, steam/C ratio = 2.5, 0.12 mol/min of glycerol flow/kg	Steam reforming of glycerol over Pt/Al_2O_3 and at high temperature (800 °C) yielded 100% gas yield. For crude glycerol, the performance was 70% of that of pure glycerol due to the presence of free fatty acids in it.	[160]
$Ni/CeZrO_2/Al_2O_3$ catalyst	Glycerin = 94 wt.%, 3-methoxy-1,2, propanediol = 6%	Yellow glycerol: H_2O = 9–3, T = 550–650 °C, O_2: yellow glycerol = 0.25–0.75	With $Ni/CeZrO_2/Al_2O_3$ catalyst, the highest H_2 selectivity and yield were 69% and 67%, respectively. The optimum conditions were 650 °C, O_2/yellow glycerol = 0.5, and H_2O/yellow glycerol = 9.	[166]
Ni–Co/Al–Mg catalyst	Glycerol = 63.17 wt.%, MeOH = 34.37 wt.%, ashes = 2.06 wt.%, water = 1.63 wt.%	400–700 °C, glycerol concentration = 10–50 wt.%, 3–17 g catalyst min/g glycerol	The optimum conditions for H_2 production were 680 °C, glycerol solution feeding of 37 wt.%, 3 g catalyst min/g glycerol. This gave 95% carbon transformation to syngas with 67 vol.% H_2.	[167]
Ni/C catalyst with MgO, La_2O_3, and Y_2O_3 promotors	Glycerol = 64 wt.%, inorganic salts = 5.7 wt.%, CH_3OH and H_2O < 5 wt.%	650 °C, 1 h, 10 °C/min, downdraft fixed bed reactor	Hydrogen (H_2) and carbon monoxide (CO) were obtained in the steam reforming over Ni-based catalyst. MgO promotor enhanced the H_2 yield by more than 80%.	[168]
Two-layered $Ni/CaO/Al_2O_3$	Glycerol = 45.2 wt.%, CH_3OH = 28.6 wt.%, FFA = 21.6 wt.%, ester and free alkali = 1.77 wt.%	600–900 °C, 0.1–2.2 MPa, 25 °C/min, fixed bed reactor	It is found that higher T and lower P are favorable for better H_2 production. The optimum conditions (700–750 °C, 0.1 MPa, H_2O/C = 1.7–2.25, C/Ca = 1) provided 0.053–0.059 mol H_2/kg.	[169]
Ni-La-Zr catalyst	Glycerol = 64 wt.%, CH_3OH and H_2O < 5 wt.%, ash = 5.7 wt.%, organic matter insoluble in glycerol = 26 wt.%	500–650 °C, 1 atm, fixed bed reactor	At 650 °C, the Ni-850 catalyst (the other being Ni-700) showed the best result for carbon conversion, which was 96%. The Ni-850 catalyst also showed lower oxidation temperature for its combustion and a lesser amount of carbon deposition.	[170]
Ni-La-Me mixed oxide catalyst; Me = Ce and/or Zr	Glycerol = 64 wt.%, inorganic salts = 5.7 wt.%, CH_3OH and H_2O < 5 wt.%, FFA% (free methyl acids) = 26%	650 °C, 10 °C/min, 1 h, fixed bed reactor	The nickel-based catalyst with both Ce and Zr showed better catalytic performance in terms of hydrogen gas yield than catalysts with either Ce or Zr alone. This catalyst was also the least prone to deactivation due to coke decomposition.	[171]
Ni-La-Ti mixed oxide catalyst	Glycerol = 64 wt.%, inorganic salts = 5.7 wt.%, CH_3OH and H_2O < 5 wt.%, polyglycerol impurities = 26 wt.%	500–650 °C, 10 °C/min, 1 h, fixed bed tubular reactor	The best values of H_2 yield and crude glycerol conversion were achieved by the Ni-La-Ti700 catalyst (the other catalyst being Ni-La-Ti850) at 650 °C. However, a slightly sharper deformation of the Ni-La-Ti700 catalyst was observed than the Ni-La-Ti850 catalyst, which was attributed to coke formation.	[172]

Table 5. An overview of catalysts used in steam reforming of glycerol for H_2 production.

Catalyst	Refs.
Ni–Mg–Al-based catalysts	[173]
Ni/Al_2O_3 and $Rh/CeO_2/Al_2O_3$	[174]
Ni/γ-Al_2O_3 catalysts	[175]
Ni-based catalysts with MgO, CeO_2, and TiO_2 supports	[176]
Co-Ni/Al_2O_3 catalyst	[177]
Nickel/nickel oxide-based catalyst	[178]
$NiO/NiAl_2O_4$ catalyst	[179]
Ni-based catalyst doped with MgO, CaO, SiO_2, Fe_2O_3, Al_2O_3	[180]
Ru/Mg (Al)O catalyst	[181]
Ruthenium catalyst with Y_2O_3, ZrO_2, CeO_2, La_2O_3, SiO_2, MgO, and Al_2O_3 as supports	[182]
Ni/Al_2O_3-ZrO_2 catalyst	[183]
Ni/CeO_2, Ni/MgO, and Ni/TiO_2 catalysts	[184]
M/CeO_2 (M = Ir, Co, Ni) catalyst	[185]
Ni/Al_2O_3 catalyst with Mg doping	[186]
LaNi-Cu-O catalyst	[187]
Cu_2O/TiO_2 catalyst	[188]
Perovskite-derived nickel-based catalysts	[189]
Rh/Al_2O_3 catalyst	[190]

3.5. Liquefaction Process

Biomass liquefaction is a valuable thermochemical conversion technology to convert biomass feedstock into liquid fuel [191]. Direct liquefaction and indirect liquefaction are the two main subcategories of this process. The indirect liquefaction of biomass refers to the conversion of feedstock into bio-oil (methyl alcohol, ethyl alcohol, dimethyl ether) by the Fischer–Tropsch synthesis process using syngas as the raw material. Direct liquefaction is further grouped into thermodynamic liquefaction and hydrolysis. Both conversion techniques convert the biomass directly into bio-oil [192]. Crude glycerol can also be converted into various liquid fuels by using the liquefaction conversion process. However, very limited research has been conducted using this technology for crude glycerol. Table 6 presents an overview of the research studies available in the literature that conducted the liquefaction process using crude glycerol as a raw material. It can be seen that most research studies used crude glycerol as a liquefaction solvent with other biomass materials to produce lignol and biopolyols. These are then utilized for the development of polyurethane foams. Polyurethane foams can then be used as a thermal insulation material. A few studies were found for the co-liquefaction of crude glycerol to produce bio-oil. It could be seen that the addition of crude glycerol to other biomass materials, such as swine manure, increases bio-oil yield. During the co-liquefaction process, the crude glycerol's constituents cause positive synergistic effects on the bio-oil yield and quality. Liquefaction is a complex process involving many different reactions such as hydrolysis, dehydration, dehydrogenation, esterification, and re-polymerization, and the reaction pathways are presently not well understood. Moreover, process optimization has to have a good balance between yield and quality of bio-oil to maximize the economics of the process, utilizing different lignocellulosic wastes as co-feed with crude glycerol.

Table 6. Summary of studies on the liquefaction/co-liquefaction of crude glycerol.

Technology	Method and Contribution	Refs.
Crude glycerol as a liquefaction solvent	Lignin from the residue of empty fruit bunches was liquefied to produce lignol. Crude glycerol was used as a liquefaction solvent in the presence of H_2SO_4. With lignol conversion of around 48%, the work suggested using the waste products from empty fruit bunches (lignin) and biodiesel (crude glycerol) to produce lignol, which can lead to development of polyurethane.	[193]
Crude glycerol as a liquefaction solvent	Saccharification from sunflower stalk residue was liquefied to produce biopolyol. Crude glycerol was used as a liquefaction solvent in the presence of H_2SO_4. With biopolyol conversion of around 60%, the work suggested using the waste products from sunflower stalk (saccharification) and biodiesel (crude glycerol) to produce biopolyol, which can lead to development of polyurethane.	[194]
Crude glycerol as a liquefaction solvent	Macroalgae (Enteromorpha) were liquefied in the presence of crude glycerol as a solvent to produce biopolyol. With biomass conversion of around 86%, the work suggested using Enteromorpha macroalgae and biodiesel waste (crude glycerol) to produce six different types of biopolyol, which can lead to development of polyurethane.	[195]
Crude glycerol as a liquefaction solvent	Corn stover was liquefied with crude glycerol as a solvent and base as a catalyst. The effect of organic impurities of crude glycerol on the production of biopolyols was investigated. The organic impurities (free fatty acids and methyl esters of fatty acids) positively affected the biopolyol production. The polyurethane foams produced from biopolyol had very good density (0.037 to 0.048 g/cm^3) and compressive strength (140 to 188 kPa).	[196]
Crude glycerol as a liquefaction solvent	Soybean straw was liquefied with crude glycerol as a solvent and H_2SO_4 as a catalyst. The effect of different liquefaction parameters (H_2SO_4 loading, temperature, biomass loading, retention time) on the production of biopolyols was investigated. It was also found that the organic impurities in the crude glycerol had a good effect on biopolyol production. Therefore, high-quality polyurethane foams were prepared from the lignocellulosic-based biopolyols.	[197]
Crude glycerol as a liquefaction solvent	Corn stover was liquefied with crude glycerol as the liquefaction solvent. The process followed a two-step method of acidic and basic catalytic treatment. The acid catalytic conversion process improved the biomass conversion, and basic catalytic conversion improved the polyol properties. The biopolyol produced polyurethane with good densities (0.04–0.05 g/cm^3) and compressive strengths (223–420 kPa).	[198]
Co-liquefaction to improve bio-oil yield	Crude glycerol was used with swine manure in a liquefaction process to evaluate its impact on the yield and properties of bio-oil. With crude glycerol as a co-substrate, the bio-oil yield increased significantly to 68% (g/g dry matter). The optimum conditions were 340 °C, 15 min residence time, and swine manure: crude glycerol = 1:3.	[199]
Co-liquefaction to improve bio-oil yield	Crude glycerol as a co-substrate in the liquefaction process was used with swine manure. The physio-chemical properties of the bio-oil were analyzed. It was found that swine manure/crude glycerol-based liquefaction produced bio-oil with lower viscosity, high H_2 content, lower pH value, and lower solid content. Moreover, the organic matter and phenol derivative were removed.	
Co-liquefaction to improve bio-oil yield	Co-liquefaction was performed with crude glycerol and swine manure. The reaction pathways associated with the co-liquefaction process were evaluated. It was found that the glycerol, CH_3OH, and H_2O had synergistic effects on the bio-oil yield. The highest bio-oil yield achieved was 79.96%.	[200]
Co-liquefaction to improve bio-oil yield	Co-liquefaction of aspen wood and crude glycerol was investigated. Aspen wood/crude glycerol co-liquefaction significantly reduced char formation. It was found that the bio-oil yield and quality was greatly influenced by feedstock composition. A reaction mechanism for glycerol was proposed.	[201]

3.6. Thermal Conversion with Supercritical Water Reforming (SCWR)

Supercritical water exists at temperatures above 370 °C and pressures higher than 221 bar [202]. By treating biomass with supercritical water, the organics in the feedstock are converted into gaseous fuels. These gaseous fuels can be condensed by cooling to room temperature [203]. The gaseous mixture produced by the supercritical water is rich in hydrogen gas. At above 600 °C, the water becomes highly oxidant and disintegrates the whole structure of the biomass material. It transfers the oxygen from water to the carbon atoms of the substrate material. As a result of this, carbon is oxidized to carbon dioxide and carbon monoxide. The hydrogen atoms from the water and substrate are bonded to form hydrogen [204]. The syngas produced by supercritical water application is different from that produced by other thermochemical conversion processes. This is mainly because syngas from the supercritical water reforming process is at high pressure, it has high H_2 content, and there is no dilution by nitrogen [205]. Crude glycerol has the potential to be converted into H_2-rich syngas through the supercritical water reforming process. Although there is great scope for this conversion process, only a small amount of research has been done thus far. Table 7 reviews the studies available in the literature that use glycerol or crude glycerol as a feedstock for syngas production using supercritical water reforming. It can be seen that hydrogen-rich gas can be produced by the supercritical water reforming of crude glycerol. Research suggests that temperature, residence time, and pressure affect the H_2 yield. The scope of this conversion technique is clear but very limited research studies have been performed. Steam reforming of crude glycerol seems challenging, and it is still far from real application as most studies are simulated.

Table 7. Studies on crude glycerol conversion using supercritical water.

Technique	Operating Conditions	Remarks	Refs.
Supercritical water reforming of glycerol was performed in a tubular reactor to produce hydrogen gas.	The operating conditions were temperature of 750–850 °C, at a pressure of 240 bar, and glycerol feed concentration between 5 and 30 wt.%. The main constituents of the dry gas were hydrogen, carbon monoxide, carbon dioxide, and methane.	Hydrogen yield of 2–4 mol H_2/mol glycerol was obtained. The most favorable conditions were high temperatures (>800 °C), longer residence time, and lower glycerol feed concentrations. Moreover, the glycerol conversion ranged from 97% to 100%, except for very high glycerol feed weight percentages (25–30 wt.%).	[206]
Supercritical water reforming (SCWR) and auto-thermal supercritical water reforming (ASCWR)	A plant of 1000 kg/h capacity was considered to be energy self-sufficient and developed on a flow sheet in Aspen Plus. ASCWR was used to assess the techno-economic analysis of hydrogen production from glycerol.	SCWR had a slightly lower energy efficiency than ASCWR but it had a smaller cost of H_2 due to less capital investment and operational complexities. The evaluation of each process led to H_2 selling price of 5.36 $/kg for SCWR and 5.75 $/kg for ASCWR.	[207]
Supercritical water co-valorization	The operating conditions were 380 °C and 230 bars. The effect of Ni-Co/Al-Mg catalyst loading (0–0.25 g catalyst/g organics) on the upgrading process was also evaluated.	The bio-oil was successfully upgraded to the following composition: carboxylic acids (R–COOH; 0–73%), furans (C_4H_4O; 0–7%), phenols (C_6H_6O; 0–85%), ketones (C_3H_6O; 0–22%), and cyclic compounds (C_nH2_n; 0–53%).	[208]
Hydrogen was produced by supercritical water treatment of crude glycerol in Aspen Plus.	A systematic thermodynamic and sensitive analysis of the reforming process was performed. The operating parameters evaluated for H_2 production were temperature, pressure, glycerol concentration, and purity of glycerol feed.	The optimum conditions found were 900 °C, 1% mole glycerol in feed. Under these conditions, a H_2 yield of 97% for crude glycerol was attained in the reformer. With water–gas shift reactions, these values approached 99%.	[209]
Hydrogen production was optimized by minimizing Gibbs free energy in Aspen Plus.	Supercritical water reforming of crude glycerol was performed. The aim was to identify the conditions suitable for the maximum production of H_2. Operating temperature, pressure, and water to glycerol mole ratio were identified as the key parameters.	A high water flow rate is required to increase the hydrogen gas. The optimum pressure is in the range of 200–300 atm. The self-sustainability of the reforming process is dependent on the crude glycerol concentration.	[210]
Hydrogen was produced by the supercritical water reforming of glycerol.	The operating conditions were 500–800 °C, 240 bar, and glycerol feed concentration between 5 and 30 wt.%. The reforming process was completed with and without an Ni-based catalyst in a tubular fixed bed reactor.	The study concluded that using the Ni-based catalyst supported with Al_2O_3 and SiO_2 the reforming temperature can be decreased to 600 °C from 800 °C for the same performance and achieving a good yield of H_2 with comparably less energy (non-catalytic reforming).	[211]
Reforming of crude glycerol was done by supercritical water to produce H_2.	The operating conditions were 450–650 °C, 6–173 s of residence time, and crude glycerol feed concentrations between 3 and 20 wt.%. The reforming gases were hydrogen, carbon dioxide, carbon monoxide, methane, and higher hydrocarbons.	Hydrogen production is linearly related with temperature and residence time. The mechanism of crude glycerol reforming was found to be dehydration of 1 mol H_2O/mole glycerol.	[212]
Methanol (CH_3OH) was produced by the supercritical water reforming of crude glycerol.	Crude glycerol was treated with simple supercritical water and supercritical water with ethyl sulfide.	The highest yield of methanol was achieved at 450 °C, 300 bar pressure, and a residence time of 30 min. It was found that the supercritical water reforming with ethyl sulfide only increased the rate of reaction and did not impact the yield of methanol.	[213]

4. Summary

Renewable sources are the best option for the sustainable and clean supply of energy to maintain modern lifestyles and industrial expansion. Renewable sources of energy are also the best option to combat the ever-increasing greenhouse gas emissions. Renewable sources of energy such as biomass, solar, and wind are the leading options with enormous potential. Thermochemical conversion processes such as gasification, pyrolysis, combustion, catalytic steam reforming, liquefaction, and supercritical water reforming use biomass as a feedstock material and produce fuel in the form of solids, liquids, and gases. These conversion processes become more economical when the feedstock is a cheap waste material. At present, most research studies focus on the utilization of agricultural waste materials as a feedstock for thermochemical conversion processes. Crude glycerol, which is a by-product of the biodiesel industry, is in extraordinary surplus quantity. Around 5 kg of crude glycerol is produced during the production of nearly 45 kg of biodiesel. Researchers around the world are now looking for ways to utilize crude glycerol so that the cost of biodiesel can be brought down. This review highlights the potential for crude glycerol to be a lucrative feedstock in thermochemical conversion processes. The review has shown the potential for an integrated biorefinery where hybrid conversion processes such as thermochemical and chemical conversion processes can co-exist.

1. There has been a lot of research using crude glycerol as a feedstock/co-feedstock with gasification technology. The results are promising in terms of having a good syngas yield. Most research has been done using fixed bed gasification technology, especially downdraft gasification technology. One reason for this could be to avoid char formation since using crude glycerol-based gasification is not yet a mature technology. Very limited research has been done with fluidized bed technology. Technical evaluation of the studies suggests that operating temperature, gasification medium, and initial crude glycerol weight percentage are the parameters influencing syngas yield.
2. A limited but reasonable amount of research has been carried out on the pyrolysis of crude glycerol. The research studies are enough to highlight the feasibility of using crude glycerol as a feedstock in the pyrolysis process. In almost all studies, crude glycerol has been used as a co-feed with another biomass material. Slow, fast, and microwave pyrolysis processes have been reported to conduct these studies. Crude glycerol co-feed ratio has been found to be an influential factor affecting bio-oil, biochar, and synthesis gas yield.
3. Although there have been very limited studies on crude glycerol combustion, there is potential for its direct combustion or co-combustion as boiler feed. Very few research studies have been done, and these are mainly on the emission patterns from crude glycerol combustion and eliminating its high auto-ignition temperature and high viscosity.
4. Catalytic steam reforming of crude glycerol has also been performed using various catalysts. Most research studies involve nickel-based catalysts. Fixed bed reactors have mostly been used. The hydrogen yield depends upon the catalytic activity and operating conditions. Very limited research has been done for steam reforming of crude glycerol, but extensive research is available in the literature for catalytic steam reforming of pure glycerol with the aim of minimizing the cost of biodiesel production.
5. Liquefaction of crude glycerol is a process to convert it into useful liquid fuel. However, most existing research has used it as a liquefaction solvent with other biomass materials to produce lignol and biopolyols. These are then utilized for the development of polyurethane foams. This is another aspect of using crude glycerol to produce insulating materials. Quite a few studies were found for the co-liquefaction of crude glycerol to produce bio-oil.
6. Hydrogen can be produced by the supercritical water reforming of crude glycerol. Research suggests that temperature, residence time, and pressure affect the H_2 yield.

The scope of this conversion technique is clear but very limited research studies have been performed.

7. Hydrothermal carbonization is another emerging thermochemical conversion process. No studies were found in this context. This process can produce hydrochar. There is obvious feasibility to use crude glycerol as a feed or co-feed in the hydrothermal carbonization process.

5. Conclusions and Future Perspective

Managing the crude glycerol from the biodiesel industry is becoming a very difficult task. With the rising level of concern about fossil fuel depletion and global warming, the biodiesel industry will continue to grow. There are still challenges in the implementation of glycerol-free processes, such as high costs and lower efficiencies, showing that these are at present immature technologies. Crude glycerol from the transesterification process requires an expensive refining process to remove impurities to make it fit for use in the production of specialty chemicals, pharmaceutics, cosmetics, emulsions, and many more products. The refining and purifying offset the profits of the products made from crude glycerol. In this scenario, utilizing crude glycerol has great potential from an energy perspective. Thermochemical conversion processes, including gasification, pyrolysis, combustion, catalytic steam reforming, liquefaction, and supercritical water reforming, have shown strong potential for utilizing crude glycerol as a feedstock/co-feedstock without any purification step. In some studies, the co-feeding of crude glycerol has been shown to have a positive impact on the product yield. Looking to the future, this review has suggested potential avenues of research for performing thermochemical conversion processes with different feedstock combinations. The co-feeding of crude glycerol with different biomass materials has different synergistic effects. The selection of reactor configuration and optimization of the process parameters need to be improved further. In processes such as catalytic steam reforming, impurities in crude glycerol can inhibit the catalytic activity. Therefore, research should be carried out on the development of novel catalysts that will not be poisoned by impurities in crude glycerol.

Author Contributions: M.R.: formal analysis, data curation, writing—original draft. A.I.: validation, writing—review and editing. B.A.-J.: methodology, validation, resources, writing—review and editing, supervision, project administration, funding. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Water and Energy Center, United Arab Emirates University (Project # 31R272 and Project # 12R014).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Long, H.; Li, X.; Wang, H.; Jia, J. Biomass resources and their bioenergy potential estimation: A review. *Renew. Sustain. Energy Rev.* **2013**, *26*, 344–352. [CrossRef]
2. Inayat, A.; Raza, M. District cooling system via renewable energy sources: A review. *Renew. Sustain. Energy Rev.* **2019**, *107*, 360–373. [CrossRef]
3. Inayat, A.; Jamil, F.; Raza, M.; Khurram, S.; Ghenai, C.; Al-Muhatseb, A.H. Upgradation of waste cooking oil to biodiesel in the presence of green catalyst derived from date seeds. *Biofuels* **2019**, *12*, 1245–1250. [CrossRef]
4. Inayat, A.; Inayat, M.; Shahbaz, M.; Sulaiman, S.A.; Raza, M.; Yusup, S. Parametric analysis and optimization for the catalytic air gasification of palm kernel shell using coal bottom ash as catalyst. *Renew. Energy* **2020**, *145*, 671–681. [CrossRef]
5. Nguyen, X.P.; Hoang, A.T.; Ölçer, A.I.; Huynh, T.T. Record decline in global CO_2 emissions prompted by COVID-19 pan-demic and its implications on future climate change policies. *Energy Sources Part A Recover. Util. Env. Eff.* **2021**, 1–4. [CrossRef]
6. Herbert, G.M.J.; Iniyan, S.; Sreevalsan, E.; Rajapandian, S. A review of wind energy technologies. *Renew. Sustain. Energy Rev.* **2007**, *11*, 1117–1145. [CrossRef]

7. Østergaard, P.A.; Mathiesen, B.V.; Möller, B.; Lund, H. A renewable energy scenario for Aalborg Municipality based on low-temperature geothermal heat, wind power and biomass. *Energy* **2010**, *35*, 4892–4901. [CrossRef]
8. Tian, X.; You, F. Carbon-neutral hybrid energy systems with deep water source cooling, biomass heating, and geothermal heat and power. *Appl. Energy* **2019**, *250*, 413–432. [CrossRef]
9. Baskar, S.; Meyrick, D.; Ramakrishnan, K.S.; Minakshi, M. Facile and large scale combustion synthesis of α-CoMoO4: Mimics the redox behavior of a battery in aqueous hybrid device. *Chem. Eng. J.* **2014**, *253*, 502–507. [CrossRef]
10. Lichty, P.; Perkins, C.; Woodruff, B.; Bingham, C.; Weimer, A. Rapid High Temperature Solar Thermal Biomass Gasification in a Prototype Cavity Reactor. *J. Sol. Energy Eng.* **2010**, *132*, 11012. [CrossRef]
11. Bai, Z.; Liu, Q.; Lei, J.; Hong, H.; Jin, H. New solar-biomass power generation system integrated a two-stage gasifier. *Appl. Energy* **2017**, *194*, 310–319. [CrossRef]
12. González-González, A.; Collares-Pereira, M.; Cuadros, F.; Fartaria, T. Energy self-sufficiency through hybridization of biogas and photovoltaic solar energy: An application for an Iberian pig slaughterhouse. *J. Clean. Prod.* **2014**, *65*, 318–323. [CrossRef]
13. Shahzad, M.K.; Zahid, A.; Rashid, T.u.; Rehan, M.A.; Ali, M.; Ahmad, M. Techno-economic feasibility analysis of a solar-biomass off grid system for the electrification of remote rural areas in Pakistan using HOMER software. *Renew. Energy* **2017**, *106*, 264–273. [CrossRef]
14. Kumaravel, S.; Ashok, S. An Optimal Stand-Alone Biomass/Solar-PV/Pico-Hydel Hybrid Energy System for Remote Rural Area Electrification of Isolated Village in Western-Ghats Region of India. *Int. J. Green Energy* **2012**, *9*, 398–408. [CrossRef]
15. Yuksel, I. As a renewable energy hydropower for sustainable development in Turkey. *Renew. Sustain. Energy Rev.* **2010**, *14*, 3213–3219. [CrossRef]
16. Singh, A.; Baredar, P. echno-economic assessment of a solar PV, fuel cell, and biomass gasifier hybrid energy system. *Energy Rep.* **2016**, *2*, 254–260. [CrossRef]
17. Aarthy, M.; Saravanan, P.; Gowthaman, M.; Rose, C.; Kamini, N. Enzymatic transesterification for production of biodiesel using yeast lipases: An overview. *Chem. Eng. Res. Des.* **2014**, *92*, 1591–1601. [CrossRef]
18. Bajaj, A.; Lohan, P.; Jha, P.N.; Mehrotra, R. Biodiesel production through lipase catalyzed transesterification: An overview. *J. Mol. Catal. B Enzym.* **2010**, *62*, 9–14. [CrossRef]
19. Silitonga, A.; Atabani, A.; Mahlia, T.M.I.; Masjuki, H.; Badruddin, I.A.; Mekhilef, S. A review on prospect of Jatropha curcas for biodiesel in Indonesia. *Renew. Sustain. Energy Rev.* **2011**, *15*, 3733–3756. [CrossRef]
20. Atabani, A.; Silitonga, A.; Badruddin, I.A.; Mahlia, T.M.I.; Masjuki, H.; Mekhilef, S. A comprehensive review on biodiesel as an alternative energy resource and its characteristics. *Renew. Sustain. Energy Rev.* **2012**, *16*, 2070–2093. [CrossRef]
21. Mofijur, M.; Masjuki, H.; Kalam, A.; Hazrat, M.; Liaquat, A.; Shahabuddin, M.; Varman, M. Prospects of biodiesel from Jatropha in Malaysia. *Renew. Sustain. Energy Rev.* **2012**, *16*, 5007–5020. [CrossRef]
22. Fukuda, H.; Kondo, A.; Noda, H. Biodiesel Fuel Production by Transesterification of Oils. *J. Biosci. Bioengineeing* **2001**, *92*, 405–416. [CrossRef]
23. Chen, J.-J.; Lee, Y.-R. Optimization of the transesterification reaction of microalgal Monoraphidium sp. *Renew. Energy* **2018**, *129*, 717–723. [CrossRef]
24. Martínez, A.; Mijangos, G.E.; Romero-Ibarra, I.C.; Hernández-Altamirano, R.; Mena-Cervantes, V.Y. In-situ transesterification of Jatropha curcas L. seeds using homogeneous and heterogeneous basic catalysts. *Fuel* **2019**, *235*, 277–287. [CrossRef]
25. Demirbas, A. Biodiesel from waste cooking oil via base-catalytic and supercritical methanol transesterificatio. *Energy Convers. Manag.* **2009**, *50*, 923–927. [CrossRef]
26. Anuar, M.R.; Abdullah, A.Z. Challenges in biodiesel industry with regards to feedstock, environmental, social and sustainability issues: A critical review. *Renew. Sustain. Energy Rev.* **2016**, *58*, 208–223. [CrossRef]
27. Monteiro, M.R.; Ambrozin, A.R.P.; Lião, L.M.; Ferreira, A.G. Critical review on analytical methods for biodiesel characterization. *Talanta* **2008**, *77*, 593–605. [CrossRef]
28. Hoang, A.T.; Nizetic, S.; Ong, H.C.; Chong, C.T.; Atabani, A. Acid-based lignocellulosic biomass biorefinery for bioenergy production: Advantages, application constraints, and perspectives. *J. Environ. Manag.* **2021**, *296*, 113194. [CrossRef] [PubMed]
29. Hoang, A.T.; Ong, H.C.; Fattah, I.R.; Chong, C.T.; Cheng, C.K.; Sakthivel, R.; Ok, Y.S. Progress on the lignocellulosic biomass pyrolysis for biofuel production toward environmental sustainability. *Fuel Process. Technol.* **2021**, *223*, 106997. [CrossRef]
30. Hoang, A.T.; Nižetić, S.; Ong, H.C.; Mofijur, M.; Ahmed, S.F.; Ashok, B.; Chau, M.Q. Insight into the recent advances of microwave pretreatment technologies for the conversion of lignocellulosic biomass into sustainable biofuel. *Chemosphere* **2021**, *281*, 130878. [CrossRef] [PubMed]
31. Hoang, A.T.; Nižetić, S.; Olcer, A.I.; Ong, H.C.; Chen, W.H.; Chong, C.T.; Thomas, S.; Bandh, S.A.; Nguyen, X.P. Impacts of COVID-19 pandemic on the global energy system and the shift progress to renewable energy: Opportunities, challenges, and policy implications. *Energy Policy* **2021**, *154*, 112322. [CrossRef]
32. Hoang, A.T.; Pham, V.V.; Nguyen, X.P. Integrating renewable sources into energy system for smart city as a sagacious strategy towards clean and sustainable process. *J. Clean. Prod.* **2021**, *305*, 127161. [CrossRef]
33. Cornejo, A.; Barrio, I.; Campoy, M.; Lázaro, J.; Navarrete, B. Oxygenated fuel additives from glycerol valorization. Main production pathways and effects on fuel properties and engine performance: A critical review. *Renew. Sustain. Energy Rev.* **2017**, *79*, 1400–1413. [CrossRef]

34. Tan, H.; Aziz, A.A.; Aroua, M.K. Glycerol production and its applications as a raw material: A review. *Renew. Sustain. Energy Rev.* **2013**, *27*, 118–127. [CrossRef]
35. Vivek, N.; Sindhu, R.; Madhavan, A.; Anju, A.J.; Castro, E.; Faraco, V.; Pandey, A.; Binod, P. Recent advances in the production of value added chemicals and lipids utilizing biodiesel industry generated crude glycerol as a substrate–metabolic aspects, challenges and possibilities: An overview. *Bioresour. Technol.* **2017**, *239*, 507–517. [CrossRef]
36. Wolfson, A.; Dlugy, C.; Shotland, Y. Glycerol as a green solvent for high product yields and selectivities. *Env. Chem. Lett.* **2006**, *5*, 67–71. [CrossRef]
37. Ardi, M.; Aroua, M.K.; Hashim, N.A. Progress, prospect and challenges in glycerol purification process: A review. *Renew. Sustain. Energy Rev.* **2015**, *42*, 1164–1173. [CrossRef]
38. Samul, D.; Serwańska-Leja, K.; Grajek, W. Impurities of crude glycerol and their effect on metabolite production. *Ann. Microbiol.* **2013**, *64*, 891–898. [CrossRef] [PubMed]
39. Leoneti, A.B.; Aragão-Leoneti, V.; de Oliveira, S.V.W.B. Glycerol as a by-product of biodiesel production in Brazil: Alternatives for the use of unrefined glycerol. *Renew. Energy* **2012**, *45*, 138–145. [CrossRef]
40. Okoye, U.; Longoria, A.; Sebastian, P.; Wang, S.; Li, S.; Hameed, B. A review on recent trends in reactor systems and azeotrope separation strategies for catalytic conversion of biodiesel-derived glycerol. *Sci. Total Environ.* **2019**, *719*, 134595. [CrossRef]
41. Monteiro, M.R.; Kugelmeier, C.L.; Pinheiro, R.S.; Batalha, M.O.; César, A. Glycerol from biodiesel production: Technological paths for sustainability. *Renew. Sustain. Energy Rev.* **2018**, *88*, 109–122. [CrossRef]
42. Rahim, S.A.N.M.; Lee, C.S.; Abnisa, F.; Aroua, M.K.; Daud, W.A.W.; Cognet, P.; Pérès, Y. A review of recent developments on kinetics parameters for glycerol electrochemical conversion—A by-product of biodiesel. *Sci. Total Env.* **2020**, *705*, 135137. [CrossRef] [PubMed]
43. Dou, B.; Song, Y.; Wang, C.; Chen, H.; Xu, Y. Hydrogen production from catalytic steam reforming of biodiesel byproduct glycerol: Issues and challenges. *Renew. Sustain. Energy Rev.* **2014**, *30*, 950–960. [CrossRef]
44. Haron, R.; Mat, R.; Abdullah, T.A.T.; Rahman, R.A. Overview on utilization of biodiesel by-product for biohydrogen production. *J. Clean. Prod.* **2018**, *172*, 314–324. [CrossRef]
45. Ng, J.-H.; Ng, H.K.; Gan, S. Recent trends in policies, socioeconomy and future directions of the biodiesel industry. *Clean Technol. Environ. Policy* **2009**, *12*, 213–238. [CrossRef]
46. Zhao, T.; Ai, J.; Wang, P.; Tong, W.; Ding, C.; Cen, Y.; Zhang, M. Research of the influence factors on transesterification reaction degree in PC/PBT blends. *Adv. Ind. Eng. Polym. Res.* **2019**, *2*, 203–208. [CrossRef]
47. Zhao, S.; Niu, S.; Yu, H.; Ning, Y.; Zhang, X.; Li, X.; Zhang, Y.; Lu, C.; Han, K. Experimental investigation on biodiesel production through transesterification promoted by the La-dolomite catalyst. *Fuel* **2019**, *257*, 116092. [CrossRef]
48. Talavera-Prieto, N.M.; Ferreira, A.G.; Moreira, R.J.; Portugal, A.T. Monitoring of the transesterification reaction by continuous off-line density measurements. *Fuel* **2019**, *264*, 116877. [CrossRef]
49. Chen, C.; Cai, L.; Zhang, L.; Fu, W.; Hong, Y.; Gao, X.; Jiang, Y.; Li, L.; Yan, X.; Wu, G. Transesterification of rice bran oil to biodiesel using mesoporous NaBeta zeolite-supported molybdenum catalyst: Experimental and kinetic studies. *Chem. Eng. J.* **2019**, *382*, 122839. [CrossRef]
50. Hegel, P.E.; Martín, L.A.; Popovich, C.A.; Damiani, C.; Leonardi, P.I. Biodiesel production from Halamphora coffeaeformis microalga oil by supercritical ethanol transesterification. *Chem. Eng. Process. Process. Intensif.* **2019**, *145*, 107670. [CrossRef]
51. Zhu, X.-N.; Wang, D.-Z.; Ni, Y.; Wang, J.-X.; Nie, C.-C.; Yang, C.; Lyu, X.-J.; Qiu, J.; Li, L. Cleaner approach to fine coal flotation by renewable collectors prepared by waste oil transesterification. *J. Clean. Prod.* **2019**, *252*, 119822. [CrossRef]
52. Izida, T.; Silva, J.; Andrade, L.; Simionatto, E.; Scharf, D.; Lima, S. Modeling transesterification reaction kinetics using fluorescence spectroscopy to interpret biodiesel production. *Chem. Eng. Sci.* **2019**, *211*, 115292. [CrossRef]
53. Pascoal, C.V.P.; Oliveira, A.L.L.; Figueiredo, D.D.; Assunção, J.C.C. Optimization and kinetic study of ultrasonic-mediated in situ transesterification for biodiesel production from the almonds of Syagrus cearensis. *Renew. Energy* **2020**, *147*, 1815–1824. [CrossRef]
54. Melchiorre, M.; Amendola, R.; Benessere, V.; Cucciolito, M.E.; Ruffo, F.; Esposito, R. Solvent-free transesterification of methyl levulinate and esterification of levulinic acid catalyzed by a homogeneous iron(III) dimer complex. *Mol. Catal.* **2020**, *483*, 110777. [CrossRef]
55. Li, H.; Liu, F.; Ma, X.; Cui, P.; Guo, M.; Li, Y.; Gao, Y.; Zhou, S.; Yu, M. An efficient basic heterogeneous catalyst synthesis of magnetic mesoporous Fe@C support SrO for transesterification. *Renew. Energy* **2020**, *149*, 816–827. [CrossRef]
56. AlSharifi, M.; Znad, H. Transesterification of waste canola oil by lithium/zinc composite supported on waste chicken bone as an effective catalyst. *Renew. Energy* **2019**, *151*, 740–749. [CrossRef]
57. Branco, K.B.; Balmant, W.; Trevisan, E.; Taher, D.M.; Mariano, A.B.; Arroyo, P.A. Phenomenological modeling of Acutodesmus obliquus microalgae in situ transesterification. *Biochem. Eng. J.* **2019**, *154*, 107434. [CrossRef]
58. Lima-Corrêa, R.A.; Castro, C.S.; Damasceno, A.S.; Assaf, J.M. The enhanced activity of base metal modified MgAl mixed oxides from sol-gel hydrotalcite for ethylic transesterification. *Renew. Energy* **2020**, *146*, 1984–1990. [CrossRef]
59. Makareviciene, V.; Gumbyte, M.; Sendzikiene, E. Simultaneous extraction of microalgae Ankistrodesmus sp. oil and enzymatic transesterification with ethanol in the mineral diesel medium. *Food Bioprod. Process.* **2019**, *116*, 89–97. [CrossRef]
60. Ong, M.Y.; Chew, K.W.; Show, P.L.; Nomanbhay, S. Optimization and kinetic study of non-catalytic transesterification of palm oil under subcritical condition using microwave technology. *Energy Convers. Manag.* **2019**, *196*, 1126–1137. [CrossRef]

61. Jung, J.-M.; Oh, J.I.; Kwon, D.; Park, Y.K.; Zhang, M.; Lee, J.; Kwon, E.E. Synthesis of fatty acid methyl esters via non-catalytic transesterification of avocado oil with dimethyl carbonate. *Energy Convers. Manag.* **2019**, *195*, 1–6. [CrossRef]
62. Nayak, S.N.; Bhasin, C.P.; Nayak, M.G. A review on microwave-assisted transesterification processes using various catalytic and non-catalytic systems. *Renew. Energy* **2019**, *143*, 1366–1387. [CrossRef]
63. Silva, L.L.; Alkimim, I.P.; Costa, J.P.; Meneghetti, S.M.; Cardoso, D. Catalytic evaluation of MCM-41 hybrid silicas in the transesterification reactions. *Microporous Mesoporous Mater.* **2019**, *284*, 265–275. [CrossRef]
64. Tanaka, S.; Nakashima, T.; Satou, N.; Oono, H.; Kon, Y.; Tamura, M.; Sato, K. Epoxide as precatalyst for metal-free catalytic transesterification. *Tetrahedron Lett.* **2019**, *60*, 2009–2013. [CrossRef]
65. Tan, S.X.; Lim, S.; Ong, H.C.; Pang, Y.L.; Fitranto, K.; Goh, B.H.H.; Chong, C.T. Two-step catalytic reactive extraction and transesterification process via ultrasonic irradiation for biodiesel production from solid Jatropha oil seeds. *Chem. Eng. Process. Process. Intensif.* **2019**, *146*, 107687. [CrossRef]
66. Lee, J.; Jung, J.-M.; Oh, J.-I.; Ok, Y.S.; Lee, S.-R.; Kwon, E.E. Evaluating the effectiveness of various biochars as porous media for biodiesel synthesis via pseudo-catalytic transesterification. *Bioresour. Technol.* **2017**, *231*, 59–64. [CrossRef] [PubMed]
67. Kialashaki, M.; Mahdavi, M.A.; Gheshlaghi, R. Improved transesterification conditions for production of clean fuel from municipal wastewater microalgae feedstock. *J. Clean. Prod.* **2019**, *241*, 118388. [CrossRef]
68. Fu, Q.; Yan, Q.; Jiang, X.; Fu, H. Heat driven self-healing isocyanate-based crosslinked three-arm Star-shaped polyglycolide based on dynamic transesterification. *React. Funct. Polym.* **2020**, *146*, 104440. [CrossRef]
69. Soliman, M.M.; Karmakar, A.; Alegria, E.C.; Ribeir, A.P.; Rúbio, G.M.; Saraiva, M.S.; da Silva, M.F.C.G.; Pombeiro, A.J. ZnO nanoparticles: An efficient catalyst for transesterification reaction of α-keto carboxylic esters. *Catal. Today* **2019**, *348*, 72–79. [CrossRef]
70. Hoang, A.T.; Le, A.T. A review on deposit formation in the injector of diesel engines running on biodiesel. *Energy Sources Part A Recover. Util. Env. Eff.* **2018**, *41*, 584–599. [CrossRef]
71. Hoang, A.T.; Tabatabaei, M.; Aghbashlo, M.; Carlucci, A.P.; Ölçer, A.I.; Le, A.T.; Ghassemi, A. Rice bran oil-based biodiesel as a promising renewable fuel alternative to petrodiesel: A review. *Renew. Sustain. Energy Rev.* **2020**, *135*, 110204. [CrossRef]
72. Hoang, A.T.; Tabatabaei, M.; Aghbashlo, M. A review of the effect of biodiesel on the corrosion behavior of metals/alloys in diesel engines. *Energy Sources Part A Recover. Util. Env. Eff.* **2019**, *42*, 2923–2943. [CrossRef]
73. Hoang, A.T.; Nižetić, S.; Ong, H.C.; Tarelko, W.; Pham, V.V.; Le, T.H.; Chau, M.Q.; Nguyen, X.P. A review on application of artificial neural network (ANN) for performance and emission characteristics of diesel engine fueled with biodiesel-based fuels. *Sustain. Energy Technol. Assess.* **2021**, *47*, 101416.
74. Mehrpooya, M.; Ghorbani, B.; Abedi, H. Biodiesel production integrated with glycerol steam reforming process, solid oxide fuel cell (SOFC) power plant. *Energy Convers. Manag.* **2020**, *206*, 112467. [CrossRef]
75. Hsu, Y.-T.; Wu, J.C.S.; Nguyen, V.-H. MgxAl-LDHs layered double hydroxides catalysts for boosting catalytic synthesis of biodiesel and conversion of by-product into valuable glycerol carbonate. *J. Taiwan Inst. Chem. Eng.* **2019**, *104*, 219–226. [CrossRef]
76. Qiu, Z.; Zhao, L.; Weatherley, L. Process intensification technologies in continuous biodiesel production. *Chem. Eng. Process. Process. Intensif.* **2010**, *49*, 323–330. [CrossRef]
77. Avhad, M.; Marchetti, J.M. A review on recent advancement in catalytic materials for biodiesel production. *Renew. Sustain. Energy Rev.* **2015**, *50*, 696–718. [CrossRef]
78. Aydın, H.; Ilkılıç, C. Effect of ethanol blending with biodiesel on engine performance and exhaust emissions in a CI engine. *Appl. Therm. Eng.* **2010**, *30*, 1199–1204. [CrossRef]
79. Singh, D.; Sharma, D.; Soni, S.; Sharma, S.; Sharma, P.K.; Jhalani, A. A review on feedstocks, production processes, and yield for different generations of biodiesel. *Fuel* **2019**, *262*, 116553. [CrossRef]
80. Effendi, A.; Gerhauser, H.; Bridgwater, T. Production of renewable phenolic resins by thermochemical conversion of biomass: A review. *Renew. Sustain. Energy Rev.* **2008**, *12*, 2092–2116. [CrossRef]
81. Goyal, H.; Seal, D.; Saxena, R. Bio-fuels from thermochemical conversion of renewable resources: A review. *Renew. Sustain. Energy Rev.* **2008**, *12*, 504–517. [CrossRef]
82. Chen, W.-H.; Lin, B.-J.; Huang, M.-Y.; Chang, J.-S. Thermochemical conversion of microalgal biomass into biofuels: A review. *Bioresour. Technol.* **2014**, *184*, 314–327. [CrossRef] [PubMed]
83. Zhang, L.; Xu, C.; Champagne, P. Overview of recent advances in thermo-chemical conversion of biomass. *Energy Convers. Manag.* **2010**, *51*, 969–982. [CrossRef]
84. Molino, A.; Chianese, S.; Musmarra, D. Biomass gasification technology: The state of the art overview. *J. Energy Chem.* **2016**, *25*, 10–25. [CrossRef]
85. Sansaniwal, S.K.; Pal, K.; Rosen, M.; Tyagi, S. Recent advances in the development of biomass gasification technology: A comprehensive review. *Renew. Sustain. Energy Rev.* **2017**, *72*, 363–384. [CrossRef]
86. Qian, K.; Kumar, A.; Patil, K.N.; Bellmer, D.D.; Wang, D.; Yuan, W.; Huhnke, R.L. Effects of Biomass Feedstocks and Gasification Conditions on the Physiochemical Properties of Char. *Energies* **2013**, *6*, 3972–3986. [CrossRef]
87. Liu, B.; Ji, S. Comparative study of fluidized-bed and fixed-bed reactor for syngas methanation over Ni-W/TiO_2-SiO_2 catalyst. *J. Energy Chem.* **2013**, *22*, 740–746. [CrossRef]
88. Rauch, R.; Hrbek, J.; Hofbauer, H. Biomass gasification for synthesis gas production and applications of the syngas. *Wiley Interdiscip. Rev. Energy Env.* **2014**, *3*, 343–362. [CrossRef]

89. Li, X.; Grace, J.; Lim, C.; Watkinson, A.; Chen, H.; Kim, J. Biomass gasification in a circulating fluidized bed. *Biomass Bioenergy* **2004**, *26*, 171–193. [CrossRef]
90. Witton, J.J.; Noordally, E.; Przybylski, J.M. Clean catalytic combustion of low heat value fuels from gasification processes. *Chem. Eng. J.* **2003**, *91*, 115–121. [CrossRef]
91. Almeidaa, A.R.A.; Ramalhoa, E.; Pilãoa, R. Crude glycerol gasification in a fixed bed gasifier. *Energy Procedia* **2018**, *153*, 149–153. [CrossRef]
92. Almeida, A.; Pilão, R.; Ramalho, E.; Ribeiro, A.; Pinho, C. Co-gasification of glycerol/fat mixtures in a downflow fixed bed reactor: Preliminary results. *Energy Rep.* **2019**, *6*, 460–465. [CrossRef]
93. Skoulou, V.K.; Zabaniotou, A.A. Co-gasification of crude glycerol with lignocellulosic biomass for enhanced syngas production. *J. Anal. Appl. Pyrolysis* **2013**, *99*, 110–116. [CrossRef]
94. Stelmachowski, M. Utilization of glycerol, a by-product of the transestrification process of vegetable oils: A review. *Ecol. Chem. Eng.* **2011**, *18*, 9–30.
95. Sabio, E.; Álvarez-Murillo, A.; González, J.; Ledesma, B.; Roman, S. Modelling the composition of the gas obtained by steam reforming of glycerine. *Energy Convers. Manag.* **2017**, *146*, 147–157. [CrossRef]
96. Suero, S.R.; Ledesma, B.; Álvarez-Murillo, A.; Al-Kassir, A.; Yusaf, T.; Cano, B.L. Glycerin, a Biodiesel By-Product with Potentiality to Produce Hydrogen by Steam Gasification. *Energies* **2015**, *8*, 12765–12775. [CrossRef]
97. Valliyappan, T. Hydrogen or Syn Gas Production from Glycerol Using Pyrolysis and Steam Gasification Processes. Master's Thesis, University of Saskatchewan, Saskatchewan, SK, Canada, 2004.
98. Yoon, S.J.; Choi, Y.-C.; Son, Y.-I.; Lee, S.-H.; Lee, J.-G. Gasification of biodiesel by-product with air or oxygen to make syngas. *Bioresour. Technol.* **2010**, *101*, 1227–1232. [CrossRef] [PubMed]
99. Sricharoenchaikul, V.; Atong, D. Fuel Gas Generation from Thermochemical Conversion of Crude Glycerol Mixed with Biomass Wastes. *Energy Procedia* **2012**, *14*, 1286–1291. [CrossRef]
100. Atong, D.; Pechyen, C.; Aht-Ong, D.; Sricharoenchaikul, V. Synthetic olivine supported nickel catalysts for gasification of glycerol. *Appl. Clay Sci.* **2011**, *53*, 244–253. [CrossRef]
101. Douette, A.M.D.; Turn, S.Q.; Wang, W.; Keffer, V.I. Experimental Investigation of Hydrogen Production from Glycerin Reforming. *Energy Fuels* **2007**, *21*, 3499–3504. [CrossRef]
102. Özgür, D.Ö.; Uysal, B.Z. Hydrogen production by aqueous phase catalytic reforming of glycerine. *Biomass Bioenergy* **2011**, *35*, 822–826. [CrossRef]
103. Valliyappan, T.; Ferdous, D.; Bakhshi, N.N.; Dalai, A.K. Production of Hydrogen and Syngas via Steam Gasification of Glycerol in a Fixed-Bed Reactor. *Top. Catal.* **2008**, *49*, 59–67. [CrossRef]
104. Hawangchu, Y.; Atong, D.; Sricharoenchaikul, V. Enhanced Microwave Induced Thermochemical Conversion of Waste Glycerol for Syngas Production. *Int. J. Chem. React. Eng.* **2010**, *8*, 1–15. [CrossRef]
105. Almeida, A.; Pilão, R.; Ribeiro, A.; Ramalho, E.; Pinho, C. Gasification of Crude Glycerol after Salt Removal. *Energy Fuels* **2019**, *33*, 9942–9948. [CrossRef]
106. Yoon, S.J.; Yun, Y.M.; Seo, M.W.; Kim, Y.K.; Ra, H.W.; Lee, J.-G. Hydrogen and syngas production from glycerol through microwave plasma gasification. *Int. J. Hydrog. Energy* **2013**, *38*, 14559–14567. [CrossRef]
107. Yus, M.; Soler, J.; Herguido, J.; Menéndez, M. Glycerol steam reforming with low steam/glycerol ratio in a two-zone fluidized bed reactor. *Catal. Today* **2018**, *299*, 317–327. [CrossRef]
108. Sricharoenchaikul, V.; Atong, D. Fluidized Bed Gasification of Glycerol Waste for Generation of Fuel Products. *J. Biobased Mater. Bioenergy* **2012**, *6*, 643–649. [CrossRef]
109. Fang, C.; Jiang, X.; Lv, G.; Yan, J.; Deng, X. Nitrogen-containing gaseous products of chrome-tanned leather shavings during pyrolysis and combustion. *Waste Manag.* **2018**, *78*, 553–558. [CrossRef]
110. Song, Q.; Zhao, H.-Y.; Xing, W.-L.; Song, L.-H.; Yang, L.; Yang, D.; Shu, X. Effects of various additives on the pyrolysis characteristics of municipal solid waste. *Waste Manag.* **2018**, *78*, 621–629. [CrossRef] [PubMed]
111. Senneca, O.; Cerciello, F.; Heuer, S.; Ammendola, P. Slow pyrolysis of walnut shells in nitrogen and carbon dioxide. *Fuel* **2018**, *225*, 419–425. [CrossRef]
112. Shi, Z.; Jin, L.; Zhou, Y.; Li, H.; Li, Y.; Hu, H. In-situ analysis of catalytic pyrolysis of Baiyinhua coal with pyrolysis time-of-flight mass spectrometry. *Fuel* **2018**, *227*, 386–393. [CrossRef]
113. Jia, C.; Chen, J.; Bai, J.; Yang, X.; Song, S.; Wang, Q. Kinetics of the pyrolysis of oil sands based upon thermogravimetric analysis. *Thermochim. Acta* **2018**, *666*, 66–74. [CrossRef]
114. Van de Velden, M.; Baeyens, J.; Brems, A.; Janssens, B.; Dewil, R. Fundamentals, kinetics and endothermicity of the biomass pyrolysis reaction. *Renew. Energy* **2010**, *35*, 232–242. [CrossRef]
115. Kan, T.; Strezov, V.; Evans, T.J. Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters. *Renew. Sustain. Energy Rev.* **2016**, *57*, 1126–1140. [CrossRef]
116. Raza, M.; Inayat, A.; Al Jaberi, B.; Said, Z.; Ghenai, C. Simulation of the pyrolysis process using blend of date seeds and coffee waste as biomass. In Proceedings of the 2020 Advances in Science and Engineering Technology International Conferences (ASET), Dubai, United Arab Emirates, 4 February–9 April 2020; pp. 1–5.
117. Collard, F.-X.; Blin, J. A review on pyrolysis of biomass constituents: Mechanisms and composition of the products obtained from the conversion of cellulose, hemicelluloses and lignin. *Renew. Sustain. Energy Rev.* **2014**, *38*, 594–608. [CrossRef]

118. Demirbas, A.; Ahmad, W.; AlAmoudi, R.; Sheikh, M. Sustainable charcoal production from biomass. *Energy Sources Part A Recover. Util. Environ. Eff.* **2016**, *38*, 1882–1889. [CrossRef]
119. Bridgwater, A.V. Review of fast pyrolysis of biomass and product upgrading. *Biomass Bioenergy* **2012**, *38*, 68–94. [CrossRef]
120. Bai, Y.; Lv, P.; Li, F.; Song, X.; Su, W.; Yu, G. Investigation into Ca/Na compounds catalyzed coal pyrolysis and char gasification with steam. *Energy Convers. Manag.* **2019**, *184*, 172–179. [CrossRef]
121. Roy, P.; Dias, G. Prospects for pyrolysis technologies in the bioenergy sector: A review. *Renew. Sustain. Energy Rev.* **2017**, *77*, 59–69. [CrossRef]
122. Zheng, Y.; Tao, L.; Yang, X.; Huang, Y.; Liu, C.; Zheng, Z. Study of the thermal behavior, kinetics, and product characterization of biomass and low-density polyethylene co-pyrolysis by thermogravimetric analysis and pyrolysis-GC/MS. *J. Anal. Appl. Pyrolysis* **2008**, *133*, 185–197. [CrossRef]
123. Zhu, P.; Luo, A.; Zhang, F.; Lei, Z.; Zhang, J.; Zhang, J. Effects of extractable compounds on the structure and pyrolysis behaviours of two Xinjiang coal. *J. Anal. Appl. Pyrolysis* **2018**, *133*, 128–135. [CrossRef]
124. Xu, Y.; Wang, T.; Ma, L.; Zhang, Q.; Wang, L. Upgrading of liquid fuel from the vacuum pyrolysis of biomass over the Mo–Ni/γ-Al2O3 catalysts. *Biomass Bioenergy* **2009**, *33*, 1030–1036. [CrossRef]
125. Bu, Q.; Lei, H.; Ren, S.; Wang, L.; Zhang, Q.; Tang, J.; Ruan, R. Production of phenols and biofuels by catalytic microwave pyrolysis of lignocellulosic biomass. *Bioresour. Technol.* **2012**, *108*, 274–279. [CrossRef]
126. Kersten, S.R.A.; Wang, X.; Prins, W.; van Swaaij, W.P.M. Biomass Pyrolysis in a Fluidized Bed Reactor. Part 1: Literature Review and Model Simulations. *Ind. Eng. Chem. Res.* **2005**, *44*, 8773–8785. [CrossRef]
127. Van Oost, G.; Hrabovsky, M.; Kopecky, V.; Konrad, M.; Hlina, M.; Kavka, T. Pyrolysis/gasification of biomass for synthetic fuel production using a hybrid gas–water stabilized plasma torch. *Vacuum* **2008**, *83*, 209–212. [CrossRef]
128. Adinberg, R.; Epstein, M.; Karni, J. Solar Gasification of Biomass: A Molten Salt Pyrolysis Study. *J. Sol. Energy Eng.* **2004**, *126*, 850–857. [CrossRef]
129. Kumar, A.; Jad, Y.E.; Collins, J.M.; Albericio, F.; de la Torre, B.G. Microwave-Assisted Green Solid-Phase Peptide Synthesis Using γ-Valerolactone (GVL) as Solvent. *ACS Sustain. Chem. Eng.* **2018**, *6*, 8034–8039. [CrossRef]
130. Zhu, X.; Zhang, Y.; Ding, H.; Huang, L.; Zhu, X. Comprehensive study on pyrolysis and co-pyrolysis of walnut shell and bio-oil distillation residue. *Energy Convers. Manag.* **2018**, *168*, 178–187. [CrossRef]
131. Manara, P.; Zabaniotou, A. Co-pyrolysis of biodiesel-derived glycerol with Greek lignite: A laboratory study. *J. Anal. Appl. Pyrolysis* **2013**, *100*, 166–172. [CrossRef]
132. Delgado, R.; Rosas, J.G.; Gómez, N.; Martínez, O.; Sanchez, M.E.; Cara, J. Energy valorisation of crude glycerol and corn straw by means of slow co-pyrolysis: Production and characterisation of gas, char and bio-oil. *Fuel* **2013**, *112*, 31–37. [CrossRef]
133. Skoulou, V.; Manara, P.; Zabaniotou, A. H2 enriched fuels from co-pyrolysis of crude glycerol with biomass. *J. Anal. Appl. Pyrolysis* **2012**, *97*, 198–204. [CrossRef]
134. Ganesapillai, M.; Manara, P.; Zabaniotou, A. Effect of microwave pretreatment on pyrolysis of crude glycerol–olive kernel alternative fuels. *Energy Convers. Manag.* **2016**, *110*, 287–295. [CrossRef]
135. Fernández, Y.; Arenillas, A.; Díez, M.A.; Pis, J.J.; Menéndez, J.A. Pyrolysis of glycerol over activated carbons for syngas production. *J. Anal. Appl. Pyrolysis* **2009**, *84*, 145–150. [CrossRef]
136. He, S.; Muizebelt, I.; Heeres, A.; Schenk, N.; Blees, R.; Heeres, H.J. Catalytic pyrolysis of crude glycerol over shaped ZSM-5/bentonite catalysts for bio-BTX synthesis. *Appl. Catal. B: Env.* **2018**, *235*, 45–55. [CrossRef]
137. Lu, J.; Liu, Z.; Zhang, Y.; Li, B.; Lu, Q.; Ma, Y.; Shen, R.; Zhu, Z. Improved production and quality of biocrude oil from low-lipid high-ash macroalgae Enteromorpha prolifera via addition of crude glycerol. *J. Clean. Prod.* **2017**, *142*, 749–757. [CrossRef]
138. Jiang, L.; Wu, N.; Zheng, A.; Wang, X.; Liu, M.; Zhao, Z.; He, F.; Li, H.; Feng, X. Effect of Glycerol Pretreatment on Levoglucosan Production from Corncobs by Fast Pyrolysis. *Polymers* **2017**, *9*, 599. [CrossRef]
139. Wu, Y.; Jiang, L.; Lin, Y.; Qian, L.; Xu, F.; Lang, X.; Fan, S.; Zhao, Z.; Li, H. Novel crude glycerol pretreatment for selective saccharification of sugarcane bagasse via fast pyrolysis. *Bioresour. Technol.* **2019**, *294*, 122094. [CrossRef]
140. Permchart, W.; Kouprianov, V.I. Permchart. Emission performance and combustion efficiency of a conical fluidized-bed combustor firing various biomass fuels. *Bioresour. Technol.* **2004**, *92*, 83–91. [CrossRef]
141. Scala, R.C.F. An SEM/EDX study of bed agglomerates formed during fluidized bed combustion of three biomass fuels. *Biomass Bioenergy* **2008**, *32*, 252–266. [CrossRef]
142. Grimm, A.; Skoglund, N.; Boström, D.; Ohman, M. Bed Agglomeration Characteristics in Fluidized Quartz Bed Combustion of Phosphorus-Rich Biomass Fuels. *Energy Fuels* **2011**, *25*, 937–947. [CrossRef]
143. Grimm, A.; Öhman, M.; Lindberg, T.; Fredriksson, A.; Boström, D. Bed Agglomeration Characteristics in Fluidized-Bed Combustion of Biomass Fuels Using Olivine as Bed Material. *Energy Fuels* **2012**, *26*, 4550–4559. [CrossRef]
144. Wiinikka, H.; Gebart, R.; Boman, C.; Boström, D.; Öhman, M. Influence of fuel ash composition on high temperature aerosol formation in fixed bed combustion of woody biomass pellets. *Fuel* **2007**, *86*, 181–193. [CrossRef]
145. Pérez, J.F.; Melgar, A.; Benjumea, P.N. Effect of operating and design parameters on the gasification/combustion process of waste biomass in fixed bed downdraft reactors: An experimental study. *Fuel* **2012**, *96*, 487–496. [CrossRef]
146. Ryu, Y.B.Y.C.; Khor, A.; Yates, N.E.; Sharifi, V.N.; Swithenbank, J. Effect of fuel properties on biomass combustion: Part I. Experiments—fuel type, equivalence ratio and particle size. *Fuel* **2006**, *85*, 1039–1046. [CrossRef]

147. Porteiro, J.; Patiño, D.; Collazo, J.; Granada, E.; Moran, J.; Miguez, J.L. Experimental analysis of the ignition front propagation of several biomass fuels in a fixed-bed combustor. *Fuel* **2010**, *89*, 26–35. [CrossRef]
148. Öhman, M.; Nordin, A. The Role of Kaolin in Prevention of Bed Agglomeration during Fluidized Bed Combustion of Biomass Fuels. *Energy Fuels* **2000**, *14*, 618–624. [CrossRef]
149. Baxter, L. Biomass-coal co-combustion: Opportunity for affordable renewable energy. *Fuel* **2005**, *84*, 1295–1302. [CrossRef]
150. Quispe, C.A.; Coronado, C.J.R.; Carvalho, J.A., Jr. Glycerol: Production, consumption, prices, characterization and new trends in combustion. *Renew. Sustain. Energy Rev.* **2013**, *27*, 475–493. [CrossRef]
151. Demirbas, M.; Balat, M. Recent advances on the production and utilization trends of bio-fuels: A global perspective. *Energy Convers. Manag.* **2006**, *47*, 2371–2381. [CrossRef]
152. Crnkovic, P.M.; Koch, C.; Ávila, I.; Mortari, D.A.; Cordoba, A.Y.M.; dos Santos, A.M. Determination of the activation energies of beef tallow and crude glycerin combustion using thermogravimetry. *Biomass Bioenergy* **2012**, *44*, 8–16. [CrossRef]
153. Bohon, M.D.; Metzger, B.A.; Linak, W.P.; King, C.J.; Roberts, W.L. Glycerol combustion and emissions. *Proc. Combust. Inst.* **2011**, *33*, 2717–2724. [CrossRef]
154. Coronado, C.R.; Carvalho, J.A.; Quispe, C.A.; Sotomonte, C.A.R. Ecological efficiency in glycerol combustion. *Appl. Therm. Eng.* **2014**, *63*, 97–104. [CrossRef]
155. Hilal-AlNaqbi, A.; Al-Omari, S.B.; Selim, M. Assessment of Tree Leaves Flakes Mixed with Crude Glycerol as a Bioenergy Source. *BioMed Res. Int.* **2016**, *2016*, 1–10. [CrossRef] [PubMed]
156. Djinovic, P.; Črnivec, I.G.O.; Erjavec, B.; Pintar, A. Influence of active metal loading and oxygen mobility on coke-free dry reforming of Ni–Co bimetallic catalysts. *Appl. Catal. B Env.* **2012**, *125*, 259–270. [CrossRef]
157. Angeli, S.; Monteleone, G.; Giaconia, A.; Lemonidou, A. State-of-the-art catalysts for CH_4 steam reforming at low temperature. *Int. J. Hydrog. Energy* **2014**, *39*, 1979–1997. [CrossRef]
158. Sehested, J. Four challenges for nickel steam-reforming catalysts. *Catal. Today* **2006**, *111*, 103–110. [CrossRef]
159. Setiabudi, H.D.; Aziz, M.A.A.; Abdullah, S.; Teh, L.P.; Jusoh, R. Hydrogen production from catalytic steam reforming of biomass pyrolysis oil or bio-oil derivatives: A review. *Int. J. Hydrog. Energy* **2019**, *45*, 18376–18397. [CrossRef]
160. Slinn, M.; Kendall, K.; Mallon, C.; Andrews, J. Steam reforming of biodiesel by-product to make renewable hydrogen. *Bioresour. Technol.* **2008**, *99*, 5851–5858. [CrossRef]
161. Delgado, D.; Minakshi, M.; Senanayake, G.; Kim, D.-J. Modified electrolytic manganese dioxide (MEMD) for oxygen generation in alkaline medium. *J. Solid State Electrochem.* **2015**, *19*, 1133–1142. [CrossRef]
162. Minakshi, M.; Blackford, M.; Ionescu, M. Characterization of alkaline-earth oxide additions to the MnO2 cathode in an aqueous secondary battery. *J. Alloy. Compd.* **2011**, *509*, 5974–5980. [CrossRef]
163. Dou, B.; Rickett, G.L.; Dupont, V.; Williams, P.T.; Chen, H.; Ding, Y.; Ghadiri, M. Steam reforming of crude glycerol with in situ CO2 sorption. *Bioresour. Technol.* **2010**, *101*, 2436–2442. [CrossRef] [PubMed]
164. Wang, C.; Dou, B.; Chen, H.; Song, Y.; Xu, Y.; Du, X.; Zhang, L.; Luo, T.; Tan, C. Renewable hydrogen production from steam reforming of glycerol by Ni–Cu–Al, Ni–Cu–Mg, Ni–Mg catalysts. *Int. J. Hydrog. Energy* **2013**, *38*, 3562–3571. [CrossRef]
165. Fermoso, J.; He, L.; Chen, D. Production of high purity hydrogen by sorption enhanced steam reforming of crude glycerol. *Int. J. Hydrog. Energy* **2012**, *37*, 14047–14054. [CrossRef]
166. Kamonsuangkasem, K.; Therdthianwong, S.; Therdthianwong, A. Hydrogen production from yellow glycerol via catalytic oxidative steam reforming. *Fuel Process. Technol.* **2012**, *106*, 695–703. [CrossRef]
167. Remón, J.; Jarauta-Córdoba, C.; García, L.; Arauzo, J. Analysis and optimisation of H2 production from crude glycerol by steam reforming using a novel two step process. *Fuel Process. Technol.* **2016**, *145*, 130–147. [CrossRef]
168. Veiga, S.; Bussi, J. Steam reforming of crude glycerol over nickel supported on activated carbon. *Energy Convers. Manag.* **2017**, *141*, 79–84. [CrossRef]
169. Chen, G.; Zhao, L. Preliminary investigation on hydrogen-rich gas production by co-steam-reforming of biomass and crude glycerin. *Int. J. Hydrog. Energy* **2012**, *37*, 765–773. [CrossRef]
170. Veiga, S.; Faccio, R.; Romero, M.; Bussi, J. Utilization of waste crude glycerol for hydrogen production via steam reforming over Ni–La–Zr catalysts. *Biomass Bioenergy* **2020**, *135*, 105508. [CrossRef]
171. Veiga, S.; Romero, M.; Faccio, R.; Segobia, D.; Duarte, H.A.; Apesteguia, C.; Bussi, J. Hydrogen-rich gas production by steam and oxidative steam reforming of crude glycerol over Ni-La-Me mixed oxide catalysts (Me = Ce and/or Zr). *Catal. Today* **2019**, *344*, 190–198. [CrossRef]
172. Veiga, S.; Faccio, R.; Segobia, D.; Apesteguía, C.; Bussi, J. Hydrogen production by crude glycerol steam reforming over Ni–La–Ti mixed oxide catalysts. *Int. J. Hydrog. Energy* **2017**, *42*, 30525–30534. [CrossRef]
173. Wang, C.; Dou, B.; Chen, H.; Song, Y.; Xu, Y.; Du, X.; Luo, T.; Tan, C. Hydrogen production from steam reforming of glycerol by Ni–Mg–Al based catalysts in a fixed-bed reactor. *Chem. Eng. J.* **2013**, *220*, 133–142. [CrossRef]
174. Adhikari, S.; Fernando, S.; Haryanto, A. Production of hydrogen by steam reforming of glycerin over alumina-supported metal catalysts. *Catal. Today* **2007**, *129*, 355–364. [CrossRef]
175. Dieuzeide, M.L.; Jobbagy, M.; Amadeo, N. Glycerol steam reforming over Ni/γ-Al2O3 catalysts, modified with Mg(II). Effect of Mg (II) content. *Catal. Today* **2013**, *213*, 50–57. [CrossRef]
176. Adhikari, S.; Fernando, S.D.; Haryanto, A. Hydrogen production from glycerin by steam reforming over nickel catalysts. *Renew. Energy* **2008**, *33*, 1097–1100. [CrossRef]

177. Sanchez, E.A.; Comelli, R.A. Hydrogen production by glycerol steam-reforming over nickel and nickel-cobalt impregnated on alumina. *Int. J. Hydrog. Energy* **2014**, *39*, 8650–8655. [CrossRef]
178. Chen, H.; Ding, Y.; Cong, N.T.; Dou, B.; Dupont, V.; Ghadiri, M.; Williams, P.T. A comparative study on hydrogen production from steam-glycerol reforming: Thermodynamics and experimental. *Renew. Energy* **2011**, *36*, 779–788. [CrossRef]
179. Dou, B.; Song, Y.; Wang, C.; Chen, H.; Yang, M.; Xu, Y. Hydrogen production by enhanced-sorption chemical looping steam reforming of glycerol in moving-bed reactors. *Appl. Energy* **2014**, *130*, 342–349. [CrossRef]
180. Dou, B.; Dupont, V.; Rickett, G.; Blakeman, N.; Williams, P.; Chen, H.; Ding, Y.; Ghadiri, M. Hydrogen production by sorption-enhanced steam reforming of glycerol. *Bioresour. Technol.* **2009**, *100*, 3540–3547. [CrossRef] [PubMed]
181. Gallo, A.; Pirovano, C.; Ferrini, P.; Marelli, M.; Psaro, R.; Santangelo, S.; Faggio, G.; Santo, V.D. Influence of reaction parameters on the activity of ruthenium based catalysts for glycerol steam reforming. *Appl. Catal. B: Env.* **2012**, *121–122*, 40–49. [CrossRef]
182. Hirai, N.-O.I.T.; Miyake, T.; Suzuki, T. Production of Hydrogen by Steam Reforming of Glycerin on Ruthenium Catalyst. *Energy Fuels* **2005**, *19*, 1761–1762. [CrossRef]
183. Iriondo, A.; Cambra, J.; Güemez, M.; Barrio, V.; Requies, J.; Sánchez-Sánchez, M.; Navarro, R. Effect of ZrO_2 addition on Ni/Al2O3 catalyst to produce H2 from glycerol. *Int. J. Hydrog. Energy* **2011**, *37*, 7084–7093. [CrossRef]
184. Adhikari, S.D.F.S.; To, S.D.F.; Bricka, R.M.; Steele, P.H.; Haryanto, A. Conversion of Glycerol to Hydrogen via a Steam Reforming Process over Nickel Catalysts. *Energy Fuels* **2008**, *22*, 1220–1226. [CrossRef]
185. Zhang, B.; Tang, X.; Li, Y.; Xu, Y.; Shen, W. Hydrogen production from steam reforming of ethanol and glycerol over ceria-supported metal catalysts. *Int. J. Hydrog. Energy* **2007**, *32*, 2367–2373. [CrossRef]
186. Dieuzeide, M.; Laborde, M.; Amadeo, N.; Cannilla, C.; Bonura, G.; Frusteri, F. Hydrogen production by glycerol steam reforming: How Mg doping affects the catalytic behaviour of Ni/Al_2O_3 catalysts. *Int. J. Hydrog. Energy* **2016**, *41*, 157–166. [CrossRef]
187. Ramesh, S.; Yang, E.-H.; Jung, J.-S.; Moon, D.J. Copper decorated perovskite an efficient catalyst for low temperature hydrogen production by steam reforming of glycerol. *Int. J. Hydrog. Energy* **2015**, *40*, 11428–11435. [CrossRef]
188. Lalitha, G.S.K.; Kumari, V.D.; Subrahmanyam, M.; Sreedhar, B.; Hebalkar, N.Y. Highly Stabilized and Finely Dispersed Cu2O/TiO2: A Promising Visible Sensitive Photocatalyst for Continuous Production of Hydrogen from Glycerol:Water Mixtures. *J. Phys. Chem. C* **2010**, *114*, 22181–22189. [CrossRef]
189. Wu, G.; Li, S.; Zhang, C.; Wang, T.; Gong, J. Glycerol steam reforming over perovskite-derived nickel-based catalysts. *Appl. Catal. B: Environ.* **2014**, *144*, 277–285. [CrossRef]
190. Chiodo, V.; Freni, S.; Galvagno, A.; Mondello, N.; Frusteri, F. Catalytic features of Rh and Ni supported catalysts in the steam reforming of glycerol to produce hydrogen. *Appl. Catal. A Gen.* **2010**, *381*, 1–7. [CrossRef]
191. Mei, D.; Liu, S.; Wang, S.; Zhou, R.; Zhou, R.; Fang, Z.; Zhang, X.; Cullen, P.J.; Ostrikov, K. Plasma-enabled liquefaction of lignocellulosic biomass: Balancing feedstock content for maximum energy yield. *Renew. Energy* **2020**, *157*, 1061–1071. [CrossRef]
192. Yang, J.; He, Q.; Yang, L. A review on hydrothermal co-liquefaction of biomass. *Appl. Energy* **2019**, *250*, 926–945. [CrossRef]
193. Lee, J.-H.; Lee, J.H.; Kim, D.-K.; Park, C.-H.; Yu, J.-H.; Lee, E.Y. Crude glycerol-mediated liquefaction of empty fruit bunches saccharification residues for preparation of biopolyurethane. *J. Ind. Eng. Chem.* **2016**, *34*, 157–164. [CrossRef]
194. Kim, K.H.; Yu, J.-H.; Lee, E.Y. Crude glycerol-mediated liquefaction of saccharification residues of sunflower stalks for production of lignin biopolyols. *J. Ind. Eng. Chem.* **2016**, *38*, 175–180. [CrossRef]
195. Kosmela, P.; Kazimierski, P.; Formela, K.; Haponiuk, J.; Piszczyk, Ł. Liquefaction of macroalgae Enteromorpha biomass for the preparation of biopolyols by using crude glycerol. *J. Ind. Eng. Chem.* **2017**, *56*, 399–406. [CrossRef]
196. Hu, S.; Li, Y. Polyols and polyurethane foams from base-catalyzed liquefaction of lignocellulosic biomass by crude glycerol: Effects of crude glycerol impurities. *Ind. Crop. Prod.* **2014**, *57*, 188–194. [CrossRef]
197. Hu, S.; Wan, C.; Li, Y. Production and characterization of biopolyols and polyurethane foams from crude glycerol based liquefaction of soybean straw. *Bioresour. Technol.* **2012**, *103*, 227–233. [CrossRef]
198. Hu, S.; Li, Y. Two-step sequential liquefaction of lignocellulosic biomass by crude glycerol for the production of polyols and polyurethane foams. *Bioresour. Technol.* **2014**, *161*, 410–415. [CrossRef] [PubMed]
199. Xiu, S.; Shahbazi, A.; Wallace, C.W.; Wang, L.; Cheng, D. Enhanced bio-oil production from swine manure co-liquefaction with crude glycerol. *Energy Convers. Manag.* **2011**, *52*, 1004–1009. [CrossRef]
200. Ye, Z.; Xiu, S.; Shahbazi, A.; Zhu, S. Co-liquefaction of swine manure and crude glycerol to bio-oil: Model compound studies and reaction pathways. *Bioresour. Technol.* **2012**, *104*, 783–787. [CrossRef]
201. Pedersen, T.H.; Jasiūnas, L.; Casamassima, L.; Singh, S.; Jensen, T.; Rosendahl, L.A. Synergetic hydrothermal co-liquefaction of crude glycerol and aspen wood. *Energy Convers. Manag.* **2015**, *106*, 886–891. [CrossRef]
202. Patcharavorachot, Y.; Chatrattanawet, N.; Arpornwichanop, A.; Assabumrungrat, S. Optimization of hydrogen production from three reforming approaches of glycerol via using supercritical water with in situ CO_2 separation. *Int. J. Hydrog. Energy* **2019**, *44*, 2128–2140. [CrossRef]
203. Ziyai, M.R.; Mehrpooya, M.; Aghbashlo, M.; Omid, M.; Alsagri, A.S.; Tabatabaei, M. Techno-economic comparison of three biodiesel production scenarios enhanced by glycerol supercritical water reforming process. *Int. J. Hydrog. Energy* **2019**, *44*, 17845–17862. [CrossRef]
204. Patcharavorachot, Y.; Saebea, D.; Authayanun, S.; Arpornwichanop, A. Hydrogen and power generation from supercritical water reforming of glycerol and pressurized SOFC integrated system: Use of different CO_2 adsorption process. *Int. J. Hydrog. Energy* **2018**, *43*, 17821–17834. [CrossRef]

205. Ortiz, F.J.G.; Campanario, F.J. Hydrogen production from supercritical water reforming of acetic acid, acetol, 1-butanol and glucose over Ni-based catalyst. *J. Supercrit. Fluids* **2018**, *138*, 259–270. [CrossRef]
206. Ortiz, F.G.; Serrera, A.; Galera, S.; Ollero, P. Experimental study of the supercritical water reforming of glycerol without the addition of a catalyst. *Energy* **2013**, *56*, 193–206. [CrossRef]
207. Galera, S.; Ortiz, F.G. Techno-economic assessment of hydrogen and power production from supercritical water reforming of glycerol. *Fuel* **2014**, *144*, 307–316. [CrossRef]
208. Remón, J.; Arcelus-Arrillaga, P.; García, L.; Arauzo, J. Simultaneous production of gaseous and liquid biofuels from the synergetic co-valorisation of bio-oil and crude glycerol in supercritical water. *Appl. Energy* **2018**, *228*, 2275–2287. [CrossRef]
209. Ortiz, F.G.; Ollero, P.; Serrera, A.; Sanz, A. Thermodynamic study of the supercritical water reforming of glycerol. *Int. J. Hydrog. Energy* **2011**, *36*, 8994–9013. [CrossRef]
210. Ortiz, F.J.G.; Ollero, P.; Serrera, A. Thermodynamic analysis of the autothermal reforming of glycerol using supercritical water. *Int. J. Hydrog. Energy* **2011**, *36*, 12186–12199. [CrossRef]
211. Ortiz, F.G.; Campanario, F.; Aguilera, P.; Ollero, P. Hydrogen production from supercritical water reforming of glycerol over Ni/Al2O3–SiO2 catalyst. *Energy* **2015**, *84*, 634–642. [CrossRef]
212. Van Bennekom, J.; Venderbosch, R.; Assink, D.; Heeres, H. Reforming of methanol and glycerol in supercritical water. *J. Supercrit. Fluids* **2011**, *58*, 99–113. [CrossRef]
213. Carr, A.G.; Shi, X.; Domene, C.; Leung, A.K.; Green, W.H. Methanol formation from the treatment of glycerol in supercritical water and with ethylsulfide. *J. Supercrit. Fluids* **2016**, *117*, 80–88. [CrossRef]