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Purifying Crude Glycerol from Biodiesel Production for Sustainable Energy Solutions

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Abstrak

Produksi biodiesel telah menjadi bagian penting dari upaya global untuk mengganti bahan bakar fosil dengan sumber energi terbarukan. Namun, salah satu masalah yang dihadapi dalam produksi biodiesel adalah peningkatan produksi gliserol sebagai produk samping. Gliserol, atau crude glycerol (CG), umumnya dihasilkan dalam jumlah signifikan dan perlu dikelola dengan bijaksana. Artikel ini membahas potensi pemanfaatan gliserol dari produksi biodiesel sebagai bahan baku untuk produksi bioetanol. Bioetanol adalah salah satu bahan bakar terbarukan yang ramah lingkungan. Penelitian ini membahas potensi transformasional gliserol dari produksi biodiesel sebagai bahan baku untuk produksi bioethanol. Beberapa kemajuan dalam teknologi pemisahan untuk memurnikan CG seperti distilasi, perlakuan kimia, dan filtrasi membrane atau ion exchange telah mendorong pengembangan konversi CG menjadi bioethanol. Dengan menggunakan metode yang telah disebutkan, kualitas crude glycerol (CG) dapat ditingkatkan dari 50% menjadi sekitar 90–95% berat. Selain itu, kemajuan dalam rekayasa genetika membuka pintu bagi pengembangan mikroorganisme yang lebih efisien dan produktif. Hal ini menciptakan peluang besar untuk mengurangi limbah, mendukung keberlanjutan sumber daya, dan mengurangi ketergantungan pada bahan bakar fosil melalui pemanfaatan gliserol sebagai bahan baku bioetanol. Konversi gliserol menjadi bioetanol merupakan langkah menuju energi terbarukan yang lebih berkelanjutan dan ramah lingkungan.

Kata Kunci: *Bioetanol, Energi terbarukan, Keberlanjutan, Rekayasa genetik*

Abstract

The production of biodiesel has become a crucial part of the global effort to replace fossil fuels with renewable energy sources. However, one of the challenges faced in biodiesel production is the increased production of glycerol as a by-product. Glycerol, or crude glycerol (CG), is generally produced in significant quantities and needs to be managed wisely. This article discusses the potential utilization of glycerol from biodiesel production as a raw material for bioethanol production. Bioethanol is one of the environmentally friendly renewable fuels. This research explores the transformative potential of glycerol from biodiesel production as a raw material for bioethanol. Progress in separation technology to purify CG, such as distillation, chemical treatment, and membrane filtration or ion exchange, has driven the development of CG conversion into bioethanol. Using the mentioned methods, the quality of crude glycerol (CG) can be improved from 50% to approximately 90–95% by weight. Furthermore, advancements in genetic engineering open the door to the development of more efficient and productive microorganisms. This creates significant opportunities to reduce waste, support resource sustainability, and decrease dependence on fossil fuels through the utilization of glycerol as a raw material for bioethanol. The conversion of glycerol into bioethanol is a step towards more.

Keywords: *Bioethanol fuel, Genetic engineering, Renewable energy, Sustainability*

Introduction

In this decade, the issue of declining availability of fossil fuels worldwide has become a prominent topic receiving widespread attention [1]–[3]. This is due to various factors leading to a common discourse on energy crises and sustainability. Global communities have grown heavily reliant on fossil fuels such as oil, coal, and natural gas to meet their energy needs. This encompasses the use of fossil fuels in transportation, electricity generation, and industry [4]–[8]. As a result, the reserves of fossil fuels, the primary source of conventional energy, continue to deplete alongside rising global demand. Furthermore, excessive use of fossil fuels has resulted in adverse environmental impacts, including greenhouse gas emissions leading to global climate change, air pollution, and environmental degradation [4], [9]–[13]. Given the decreasing availability of fossil fuels and increasing environmental impacts, many countries have developed long-term sustainable energy plans. These plans include objectives to reduce dependence on fossil fuels, improve energy efficiency, and promote the use of renewable energy sources. Biodiesel is an example of how Indonesia, along with other countries, is striving to reduce its reliance on fossil fuels and move toward more sustainable and environmentally-friendly energy sources [14]–[17]. Through policies, innovation, and investments, biodiesel has become a significant choice in Indonesia's energy diversification efforts [18].

Biodiesel consumption worldwide, including in Indonesia, has experienced significant annual growth. This increase is in line with the growing number of vehicles and efforts to reduce dependence on fossil fuels [18]–[20]. However, the main issue in biodiesel production is that during the transesterification reaction to convert vegetable oil or fats into biodiesel, glycerol is also produced as a byproduct [19], [21]–[23]. Most biodiesel production methods generate glycerol in approximately 10% by weight of the biodiesel produced, meaning that for every 100 kg of biodiesel produced, 10 kg of glycerol is also generated [22], [24], [25]. According to previous researchers, the glycerol market is highly responsive to the increasing availability of glycerol in the market [22], [26], [27]. Furthermore, waste glycerol from biodiesel production can pose environmental pollution problems if not addressed. Hence, numerous research and industrial efforts are focused on developing ways to utilize and purify the generated glycerol, as well as exploring various applications for glycerol to prevent it from becoming waste. These reasons have drawn the attention of researchers to develop technologies to utilize glycerol, including its conversion into valuable energy products [14], [28]–[30].

Glycerol, also known as glycerin or 1,2,3-propanetriol, is a three-carbon molecule with a hydroxyl group on each carbon. It can be easily modified by reacting with the hydroxyl (-OH) groups [31]. The glycerol referred to in this article is the main byproduct of the transesterification reaction of fats or vegetable oils, such as sunflower oil, peanut oil, olive oil, soybean oil (in the United States) [32], [33], rapeseed oil, sunflower oil (in Europe) [34], palm oil in Southeast Asia (primarily Malaysia and Indonesia) [35]–[37], and coconut oil (in the Philippines) [38], to produce biodiesel.

Recently, the interest of researchers in the conversion of biomass into bioethanol as an energy product through fermentation has increased [39]–[42]. This is due to the sustainability and efficiency potential of this process in bioethanol production. Bioethanol is an alternative fuel produced from renewable sources, namely carbon-containing materials such as sugar or biomass. Glycerol, as one of the biomass sources, has an advantage because it contains a carbon source that can be directly converted into ethanol by specific microorganisms [23], [30], [43]–[46]. This allows for bypassing the hydrolysis step required by some other feedstocks sourced from lignocellulosic biomass in the second generation [40], [47]. Using glycerol as a feedstock is expected to reduce the reaction time needed to produce bioethanol. This can enhance production efficiency and reduce overall costs. The use of glycerol as a feedstock can also result in a higher yield, meaning that more bioethanol can be produced from a given amount of glycerol [25], [31], [48].

Unfortunately, one of the challenges faced in using glycerol from biodiesel waste is its initial purity. Glycerol from biodiesel waste tends to have low purity, ranging from 40 to 55% by weight [39], [49]. To make this glycerol suitable for bioethanol production, a purification process is required such as distillation, chemical treatment, and membrane filtration or ion exchange. Glycerol can be purified from other contaminants like water, methanol, and catalytic salts using various purification techniques, including distillation, chemical treatment, membrane technology, and ion-exchange [50], [51]. Distillation is one of the commonly used methods to separate glycerol from other components [52]. Chemical treatment may involve chemical reactions to eliminate contaminants [53]. Membrane technology and ion-exchange involve the use of membranes and ion-exchange resins to separate glycerol from contaminants [50], [52]. After the purification process, glycerol can achieve a much higher purity, typically around 90 to 95% by weight. Higher purity allows this glycerol to be used more efficiently in bioethanol production.

Methodology

The method used in this study is a comprehensive literature review that involves extensive and in-depth research on the potential of crude glycerol from biodiesel production waste as a raw material for bioethanol especially in the purification of glycerol. A wide-ranging and diverse array of information sources includes research reports, conference proceedings, and relevant scientific articles, including those related to the purification of crude glycerol.

Potential of Crude Glycerol

The transesterification of vegetable or animal fats is a crucial chemical process employed in the production of biodiesel, a highly sought-after fuel for several compelling reasons. Biodiesel's appeal stems from its renewable nature, which contributes to reducing our reliance on finite fossil fuel resources [54], [55]. Moreover, biodiesel is celebrated for its environmentally friendly attributes, as it significantly reduces greenhouse gas emissions and air pollutants when compared to traditional petroleum-based fuels [56]–[59]. Additionally, biodiesel is known for its low toxicity, making it a safer and less hazardous option for both human health and the environment [60], [61].

This intricate process involves the transformation of vegetable or animal fats into biodiesel through a series of transesterification reactions. These reactions typically involve the use of alcohols, with methanol or ethanol being the common choices [20]. During this process, the triglycerides present in the fats are chemically modified to produce biodiesel, while the byproduct of this transformation is glycerol [62]. Glycerol is produced as a co-product, with its volume accounting for approximately 10% of the total biodiesel production [22], as illustrated in Figure 1[63], [64].

The generation of glycerol as a co-product is an integral aspect of biodiesel production, and the effective management and utilization of this glycerol co-product have garnered considerable attention in recent years [22], [26], [62]. This attention has primarily revolved around exploring ways to maximize the value of glycerol, not only as an integral part of the biodiesel production process but also as a valuable resource for various other applications, including its potential role as a precursor in the production of bioethanol. The strategic management of glycerol co-product opens up new avenues for achieving sustainability in the biodiesel production process and reinforces its position as a pivotal player in the transition towards cleaner and more environmentally responsible energy solutions [65].

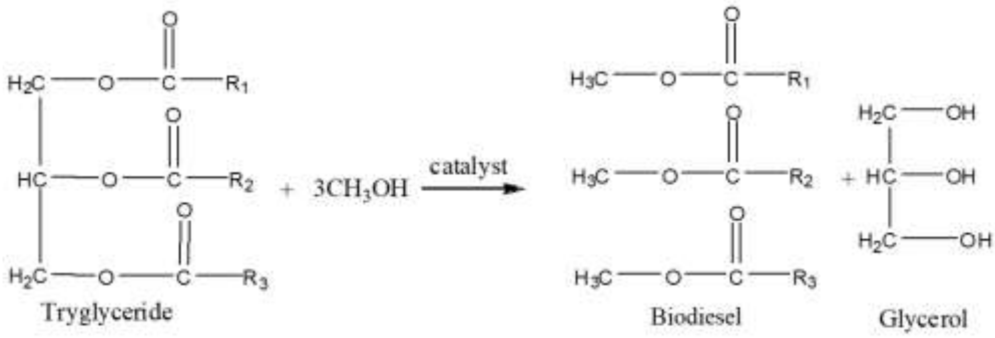

Figure 1. Transesterification Reaction Scheme [66]

Purified glycerol presents a promising opportunity to play a pivotal role in a wide array of energy conversion processes. Its versatility enables the diversification of feedstock utilization derived from glycerol, thus unlocking the full spectrum of its advantages. By incorporating purified glycerol into various energy conversion processes, we embrace a sustainable and efficient approach to waste management and resource utilization. This approach is not only environmentally responsible but also economically viable [49].

The utilization of purified glycerol in diverse energy conversion processes signifies a concerted effort to transition towards cleaner and more sustainable energy sources. It acts as a testament to our commitment to addressing global challenges related to emissions and environmental impacts [67], [68]. The positive contributions of purified glycerol extend beyond energy production, reaching towards a broader vision of a greener and more sustainable future. Figure 2 [31]provides a visual representation of the numerous energy products that can be harnessed from glycerol, further underscoring its significance in our journey towards a cleaner and more eco-friendly energy landscape [69].

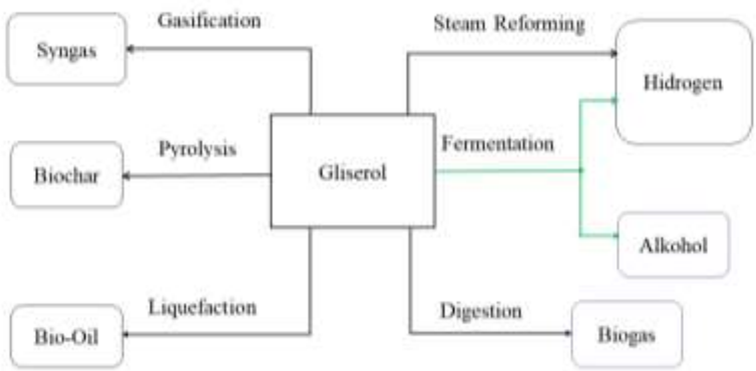

Figure 2. Diagram of Glycerol Conversion Pathway into Various Energy Products [31]

As previously elucidated, the production of glycerol has experienced a significant surge, primarily driven by the ever-increasing global production of biodiesel [70]. This surge is intrinsically linked to the continual expansion of biodiesel production capacity, which, in turn, results in a substantial upswing in the production of crude glycerol. To put this into perspective, by the year 2020, the production of crude glycerol had reached an impressive figure of approximately 5.8 billion pounds, a fact that is visually represented in Figure 3 as outlined in the study conducted by [69].

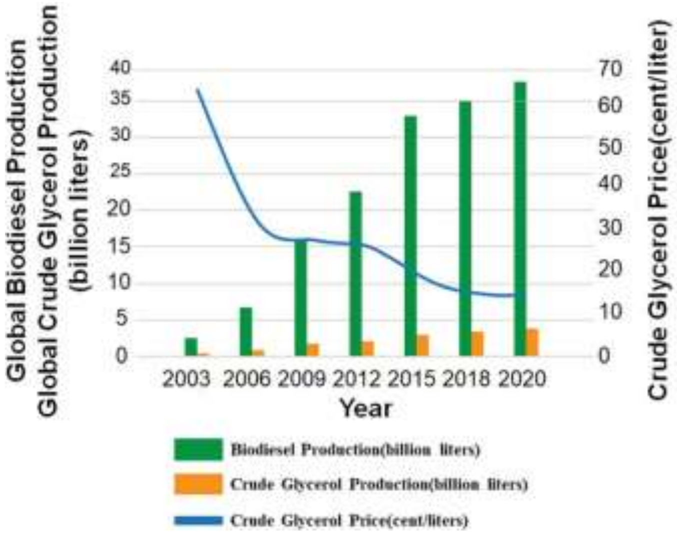

Figure 3. Global biodiesel and crude glycerol production from 2003 to 2020[69]

The consistent and upward trajectory of glycerol production is not without its challenges. One of the foremost challenges stems from the potential accumulation of surplus glycerol, which can pose logistical and environmental concerns if not effectively managed [49]. It is therefore imperative to explore strategies for the purposeful utilization or management of this surplus glycerol, and one such strategy is the conversion of glycerol into alternative products, with bioethanol emerging as a promising option [71]. This multifaceted approach not only addresses the challenge of glycerol surplus but also aligns with the broader goals of sustainability and resource optimization, offering a tangible solution to the burgeoning biodiesel industry's byproduct challenge.

Distillation Method

The distillation method is one of the techniques employed in the purification of crude glycerol (CG), which is a byproduct in biodiesel production [52], [72]. Distillation is a process for separating components within a mixture based on their differences in boiling points. In the case of purifying crude glycerol, distillation is used to separate glycerol from other substances that may be present in the mixture, such as water, methanol, catalytic salts, and other impurities. The following are the stages of the distillation method in the purification of crude glycerol from biodiesel production waste:

The stage of crude glycerol preparation: Before distillation, crude glycerol needs to be prepared. This may involve filtration or coarse separation to remove coarse particles or other solid substances that may be present in crude glycerol [24]. Simple distillation stage: This stage is used to remove components with lower boiling points, such as methanol. It is done by heating crude glycerol in a closed container. As the mixture is heated, the methanol component will evaporate earlier and then condense back into a liquid form [26], [73]. Fractionation stage: In this stage, glycerol components with higher boiling points will settle at the bottom of the column, while water components will evaporate to the top of the column and then condense back into liquid [74]. Purification stage: After distillation is completed, the fraction containing pure glycerol can be separated from other unwanted components, such as water and catalytic salts [20]. This stage may use separation equipment, such as centrifugation or filtration, to remove precipitates or other solid substances that may be present in the mixture. In addition, deionization or desalination can also be used to remove impurity ions or remaining salts in pure glycerol. The distillation method generally produces glycerol with a purity of about 95% or higher [51].

Chemical Treatment Method

The chemical treatment method represents yet another viable approach for refining crude glycerol (CG), a byproduct stemming from biodiesel production [53]. In this method, specific chemicals are deployed to eliminate impurities and yield a purer form of glycerol. Notably, chemicals like sulfuric acid or phosphoric acid are introduced into the crude glycerol[75]. These chemicals initiate interactions with the impurities present, giving rise to compounds that can be readily separated. To elaborate further, during the chemical reaction, the impurities engage with the chemicals and form intricate compounds that can be precipitated. The resultant precipitate is subsequently separated through the utilization of a centrifuge or filtration process [76]–[78].

By employing the chemical treatment method, it is conceivable to achieve glycerol purities typically ranging from 90% to 95% [21], [79]. This method underscores the significance of chemical processes in enhancing the quality of glycerol derived from biodiesel production, paving the way for a variety of valuable applications while effectively addressing the challenges associated with impurity removal.

Membrane and Ion-Exchange Methods

The utilization of membrane technology in conjunction with the ion exchange method represents a highly effective approach to purifying crude glycerol (CG), an inevitable byproduct in the biodiesel production process [26], [77]. This combined approach offers a versatile means of eliminating a diverse range of impurities that may be present in crude glycerol. These impurities encompass substances like salts, ions, and undesirable organic compounds. The synergy between membrane technology and ion exchange techniques allows for the comprehensive removal of these unwanted elements, resulting in a significantly enhanced level of glycerol purity. This refined glycerol can subsequently be harnessed for various valuable applications, making it a valuable resource derived from biodiesel production [80], [81].

Membrane technology is a versatile method employed to separate molecules based on their respective size, charge, or physical characteristics. When it comes to purifying CG, specific membranes are designed to selectively remove various impurities from glycerol [50], [52], [53]. For example, ultrafiltration membranes are used to effectively eliminate solid particles and large molecules, while nanofiltration membranes come into play when the objective is to remove salts and small organic compounds. The process of separation through membrane technology offers a spectrum of glycerol purities, contingent upon the particular type of membrane employed. Ultrafiltration membranes generally yield glycerol with purities in the range of approximately 90% to 95% [82], while nanofiltration membranes can achieve purities surpassing 95% [83], [84]. This adaptability makes membrane technology an invaluable tool in refining crude glycerol and enhancing its usability in various applications.

The ion exchange process is a technique that employs specific resins or ion exchange materials with the ability to capture and replace particular ions present in crude glycerol (CG). This process is invaluable for eliminating undesired salts and ions effectively. Cation exchange resins are typically utilized to eliminate positively charged ions (cations), while anion exchange resins are used to remove negatively charged ions (anions) [81].

During ion exchange, the resins or materials function as selective traps for the targeted ions. As the CG is passed through these materials, the undesirable ions are captured and exchanged for other ions that are less problematic or are more easily separated. This process significantly enhances the purity of glycerol, often achieving levels exceeding 95% [75]. Consequently, glycerol refined through the ion exchange method becomes highly suitable for a wide range of applications, particularly those that require stringent purity standards. It is an efficient and reliable approach to improve the quality of crude glycerol for diverse industrial and commercial purposes [85].

Bioethanol

Bioethanol is a renewable source of energy because its raw material can be naturally replenished through agriculture. This is a primary advantage in efforts to reduce dependence on fossil fuels and lower carbon emissions [55]. Bioethanol is used as a fuel for motor vehicles, particularly when blended with gasoline [86]. The mixture of bioethanol with gasoline is often referred to as E10 (10% bioethanol) or E85 (85% bioethanol), depending on the percentage of ethanol in the blend [87].

Bioethanol is produced from the fermentation of biomass involving a biochemical process in which microorganisms such as yeast or bacteria convert the sugars and carbohydrates present in biomass into ethanol (bioethanol) and carbon dioxide [88], [89]. Various microorganisms from fungi and bacteria can be used to convert sugars into ethanol. Saccharomyces cerevisiae (yeast) is the most commonly used fungus [90], [91], while bacteria that can be used include Zymomonas mobilis, Escherichia coli (E. coli), and Kluyveromyces spp [44], [46], [92]. Then, ethanol as the fermentation product can be separated and purified through the distillation process [52]. The choice of the right microorganism depends on the source of sugar to be converted into ethanol, as well as industrial needs and sustainability considerations. Some microorganisms have higher tolerance to alcohol or acidity, while others have a better capacity to convert specific types of sugars. Therefore, in bioethanol production, the selection of microorganisms is crucial for optimizing yield and efficiency [43].

Several challenges are associated with bioethanol production, particularly in terms of competition with food production, land use, and the sustainability of feedstock sources [93]. However, the utilization of glycerol (CG) as a feedstock originating from biodiesel production waste can be one of the solutions to address some of these challenges. By using glycerol from biodiesel production waste as a feedstock, there is no need for additional land or resources that would compete with food production [69]. The utilization of glycerol from biodiesel production waste is an example of how the renewable energy industry can integrate waste from one production process into a feedstock for another, creating more sustainable and environmentally friendly solutions. This approach can also help reduce environmental impacts and enhance efficiency within the renewable energy production chain [93].

Up to now, the production of bioethanol derived from first to third-generation biomass has developed and varies depending on location, technology, and resources used. Production of bioethanol from first-generation biomass, such as sugarcane, corn, and wheat, can reach around 60-70 billion liters per year worldwide [93], [94]. Some countries like the United States, Brazil, and Europe have become major producers of bioethanol from these first-generation sources. Meanwhile, the production of bioethanol from second-generation biomass, such as straw, wood, and algae, has faced many challenges in development, and the production volume is lower than the first generation, approximately 5-10 billion liters per year worldwide [94]. Furthermore, third-generation biomass, including algae and marine plants, is still in early stages of research and development, and its production is currently limited. Even the production of bioethanol from fourth-generation biomass is still in early research and development stages and has not yet reached significant commercial production levels [95]. Fourth-generation bioethanol development plans are a more recent concept that includes the utilization of CG. The technology is designed with genetic engineering techniques to enhance productivity and efficiency in bioethanol production. Sources of biomass from various generations are presented in Table 1.

Table 1. Sources of biomass from various generations

Biomass Sources	wt. %			References
	Cellulose	Hemicelluloses	Lignin	
Wood	35-50	20-30	25-30	[96]
Straw	33-40	20-25	15-20	[97]
Sugarcane Bagasse	19-24	32-48	23-32	[98]
Corncob	50.5	31	15	[99]
Scrap paper	60-70	10-20	5-10	[100]
Leaf	15-20	80-85	-	[101]
Algae	13-14	14-15	14	[32]

Conclusion

The global push towards renewable energy sources has underscored the important role of biodiesel production in replacing fossil fuels. However, the surge in production of the by-product glycerol poses a major challenge. This study has investigated the potential for the transformation of glycerol from biodiesel production into a raw material for bioethanol production. By strategically optimizing the fermentation process and utilizing purification technologies such as distillation, chemical treatment, and membrane filtration, glycerol can be efficiently converted into bioethanol. The important progress achieved in increasing the purity of crude glycerol (CG) from 50% to approximately 90–95 wt.% further emphasizes the feasibility and opportunities of this approach.

The conversion of glycerol to bioethanol is emerging as a promising step towards achieving a more sustainable and environmentally friendly renewable energy landscape. The comprehensive integration of purification methods, advances in genetic engineering, and effective utilization of glycerol as a bioethanol feedstock marks a significant step in overcoming the challenges associated with managing glycerol byproducts. Thus, the potential for glycerol conversion has become a hope for more environmentally friendly energy solutions.

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