Purification and Utilization of Glycerol as Biodiesel By-Product: Valorization Approach

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Abstract:
Glycerol (also known as glycerin) is a major byproduct in the biodiesel manufacturing process. In general, for every 10 pounds of biodiesel produced, approximately 1 pounds of crude glycerol are created. Along with biodiesel manufacture increase, a large surplus of glycerol is being produced. Purification of crude glycerol and its further conversion/utilization play an important role in bio-fuels industry. In this article, purification and utilization of glycerol as biodiesel by-Product as valorization approach are discussed and proposed for improving biodiesel manufacture.

1 Introduction

Glycerol (glycerine or glycerin) is a simple polyol compound, which is a colorless, odorless, viscous liquid that is sweet-tasting and non-toxic. The glycerol backbone is found in all lipids known as triglycerides. [1] It is widely used in the food industry as a sweetener and humectant and in pharmaceutical formulations. [2] Glycerol has three hydroxyl groups that are responsible for its solubility in water and its hygroscopic nature. [3, 4, 5, 6, 7]

Glycerol is generally obtained from plant and animal sources where it occurs as triglycerides. Triglycerides are esters of glycerol with long-chain carboxylic acids. The hydrolysis, saponification, or transesterification of these triglycerides produces glycerol as well as the fatty acid derivative, as shown in Figure 1.

Glycerol is used to produce nitroglycerin, which is an essential ingredient of various explosives such as dynamite, gelignite, and propellants like cordite. [8, 9] Reliance on soap-making to supply co-product glycerol made it difficult to increase production to meet wartime demand. Hence, synthetic glycerol processes were national defense priorities in the days leading up to World War II. Nitroglycerin, also known as glycercyl trinitrate (GTN) is commonly used to relieve angina pectoris, taken in the form of sub-lingual tablets, or as an aerosol spray. Allyl iodide, a chemical building block for polymers, preservatives, organometallic catalysts, and pharmaceuticals, can be synthesized by using elemental phosphorus and iodine on glycerol. A great deal of research is being conducted to try to make value-added products from crude glycerol (typically containing 20% water and residual esterification catalyst) obtained from biodiesel production. The
use of crude glycerol as an additive to biomass for a renewable energy source when burned or
gasified is also being explored. A few examples are shown below: Hydrogen gas production unit
Glycerine acetate (as a potential fuel additive); Conversion to propylene glycol; Conversion to
acrolein; Conversion to ethanol; Conversion to epichlorohydrin, a raw material for epoxy resins.
[10, 11] In this paper we will discuss purification and utilization of glycerol as biodiesel by-Product
as valorization approach.

2 Crude Glycerol Purification

Purification of crude glycerol is essential for its applications for high-value products. [12] Purifica-
tion is required to transform crude glycerin to a usable state for existing or emerging uses. [13] The purity requirements for the emerging applications of glycerin vary, and are often intermediate
to the crude and refined grades previously established for the classical applications. [14] The salt
content in crude glycerin, stemming from the use of homogeneous alkaline catalysts, [15, 16] of-
ten ranges from 5 percent to 7 percent, which makes conventional techniques cost intensive. [17] This suggests that for future glycerin markets a new low-cost purification strategy may be more
cost-effective than conventional routes. [18]

The glycerin produced in the transesterification of triglycerides reaction is a crude grade. [19,
20] Almost all biodiesel production today involves homogeneous alkaline catalysts such as sodium
methylate. The transesterification of triglycerides with methanol generates a methyl-ester phase
and a glycerin phase. Impurities such as catalyst, soap, methanol and water are preferentially
concentrated in the glycerin phase. The glycerin phase is typically neutralized with acid and the
cationic component of the catalyst is incorporated as a salt.

3 Catalytic Conversion of Glycerol

The conversion of glycerol has been the focus of extensive research as it is a highly functionalized
molecule readily derived from biomass. One desirable target is to convert glycerol into methanol,
which is a major chemical intermediate of immense utility. However, the central problem for the
conversion of glycerol into methanol is that hydrogen has to be introduced. [21, 22] We wanted
to explore the reactivity of glycerol using water as a potential hydrogen source specifically under
conditions in which synthesis gas is not required as a key intermediate.

These conversions include steam reforming, aqueous-phase reforming, hydrogenolysis, ox-
idation, dehydration, esterification, etherification, carboxylation, acetalization, and chlorination.
[23, 24] Typical products are hydrogen, propanediols, dihydroxyacetone, glyceric acid, acrolein,
glyceride, polyglycerol, glycerol carbonate, acetals, ketals, and epichlorohydrine. Recent studies
on the catalysts, reaction conditions, and possible pathways are primarily discussed. They indicate
that major breakthroughs are achieved by the use of multifunctional catalysts, [25, 26] process in-
tensification and integrated reactions. Literature survey suggests that future work on the catalytic conversion of glycerol for commercial goals particularly requires new catalysts, innovative reactor engineering, and close multidisciplinary partnership. [27, 28]

Substantial production of oxygenates from biomass conversion and biodiesel production create interest in upgrading these compounds to gasoline range products, among others. Glycerol is the byproduct of biodiesel production and also is a model for polyol sugar compounds in biomass. [29, 30, 31] In order to utilize glycerol, dehydration and oligomerization over acidic zeolites is proposed. It was found that glycerol can be directly converted to aromatics up to 60% yield on H-ZSM5 (Si/Al=45) via a well known oligomerization process. [32]

4 Concluding Remarks

In the present work, purification and utilization of glycerol as biodiesel by-product as valorization approach are discussed. It is concluded that efficient purification method of crude glycerol and catalytic conversion of glycerol are valuable approach for valorization biodiesel manufacture.

5 Acknowledgments

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References


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Figure 1: Transesterification Reaction for Biodiesel and Glycerol Production
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Catalog: Unit Operation

Chemical Engineers Organization  Chemical engineering is a branch of engineering that applies physical sciences (physics and chemistry), life sciences (microbiology and biochemistry), together with applied mathematics and economics to produce, transform, transport, and properly use chemicals, materials and energy. A chemical engineer designs large-scale processes that convert chemicals, raw materials, living cells, microorganisms and energy into useful forms and products. Chemical engineers are involved in many aspects of plant design and operation, including safety and hazard assessments, process design and analysis, control engineering, chemical reaction engineering, construction specification and operating instructions.

Other Catalogs:

Unit Operation
Thermodynamics
Kinetics
Process Engineering

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