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RAW GLYCEROL RE-VALUING THROUGH ETHERIFICATION WITH
ISOBUTYLENE: PROCESS DESIGN AND TECHNO-ECONOMICAL ASSESSMENT
 --Manuscript Draft--

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Abstract:	This study evaluates the techno-economic feasibility to produce tert-butyl ethers of glycerol in Colombia using glycerol obtained from biodiesel production. The major drawback of this process is related to the high costs associated to the isobutylene reagent used for this reaction. Three possible scenarios, using isobutylene: glycerol molar ratios of 2:1 and 4:1, have been evaluated by simulation and techno-economical assessment using pure isobutylene, C4 fraction and a mixture of C4 and isobutylene as well as a refining stage for crude glycerol. The desired product, a mixture of di- and tri- ethers of glycerol (h-GTBE) was obtained in high amounts for the three scenarios (92 - 99 wt %) and a direct relation between production cost and raw material cost was established. The prices for h-GTBE were higher than the proposed selling prices; however, the formation of byproduct (C4 fraction) can make the process competitive. h-GTBE production did not have a competitive price for any scenario at high isobutylene: glycerol molar ratio. The production price was lowered by around 20% for all scenarios when crude glycerol was considered. Finally, competitive price of h-GTBE (0.96 \$/kg) and NPV positive was obtained using a mixture of C4 and isobutylene and crude glycerol.
Suggested Reviewers:	Jonathan Moncada, Ph.D Researcher, Delft University of Technology: Technische Universiteit Delft J.MoncadaBotero@tudelft.nl Expert in the simulation and sustainable process Mariano Martín, Ph.D Researcher, Universidad de Salamanca mariano.m3@usal.es He working in the topic (simulation, integration, biofuel production) Moshe Rosenberg, Ph.D Universidad Autónoma de Baja California: Universidad Autonoma de Baja California mrosenberg@ucdavis.edu Expert in simulation process



Bogotá-Colombia, August 28th, 2020

Dear Editor.

Journal of Industrial and Engineering Chemistry.

Please find attached a copy of the manuscript entitled "**RAW GLYCEROL RE-VALUING THROUGH ETHERIFICATION WITH ISOBUTYLENE: PROCESS DESIGN AND TECHNO-ECONOMICAL ASSESSMENT**", to be considered for publication in *Journal of Industrial and Engineering Chemistry*.

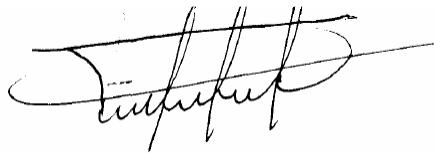
We would like to submit for your consideration our most recent study on the production of Tert-butyl ethers of glycerol (h-GTBE) through etherification with isobutylene. In this work, the viability of producing h-GTBE in Colombia using glycerol from biodiesel production is carried out with the goal to transform the glycerol into high added-value products (due to the increase of it from biodiesel manufacture). In this work, a techno-economic assessment was carried out considering different configuration, specifically, varying the sources of raw materials as well the relation of fed. As result final the production cost has been mainly related to the raw material prices. We believe that this work shows interesting alternatives to improve aalternative sources of renewable fuels in the Colombian context. We hope that our work will receive attention by academics and can contribute research in field of processing.

Finally, the authors state that the submitted work was not published previously and it is not under consideration for publication elsewhere, and if accepted it will not be published elsewhere in substantially the same form, in English or in any other language, without the written consent of the Publisher. All authors have approved this submission. The least 5 papers cited in our manuscript (published within the past 18 months) that working in the topic are presented:

1. F. Chang, Q. Zhou, S. X. Pan, Y. He, Catalytic upgrading of glycerol, a promising biodiesel coproduct. In Biomass, Biofuels, Biochemicals (2020) (pp. 395-405). Elsevier. <https://doi.org/10.1016/B978-0-444-64307-0.00015-9>
2. S. Veluturla, N. Archana, D. Subba Rao, N. Hezil, I. S. Indrajaya, S. Spoorthi, Catalytic valorization of raw glycerol derived from biodiesel: a review. Biofuels, 9(3) (2018) 305–314. <https://doi.org/10.1080/17597269.2016.1266234>

3. Ö. D. Bozkurt, F. Yılmaz, N. Bağlar, S. Çelebi, A. Uzun, Compatibility of di-and tri-tert-butyl glycerol ethers with gasoline. Fuel (2019), 255, 115767. <https://doi.org/10.1016/j.fuel.2019.115767>
4. S. T. S Veras, P. Rojas, L. Florencio, M. T. Kato, J. L. Sanz, Production of 1, 3-propanediol from pure and crude glycerol using a UASB reactor with attached biomass in silicone support. Bioresource technology, 279 (2019), 140-148. <https://doi.org/10.1016/j.biortech.2019.01.125>
5. J. Lu, T. Chen, Y. Jiang, W. Zhang, W. Dong, W, J. Zhou, F. Xin, The draft genome sequence of Clostridium sp. strain CT7, an isolate capable of producing butanol but not acetone and 1, 3-propanediol from crude glycerol. 3 Biotech (2019), 9(2), 63. <https://doi.org/10.1007/s13205-019-1598-7>.

Best Regards,



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Declaration of interests

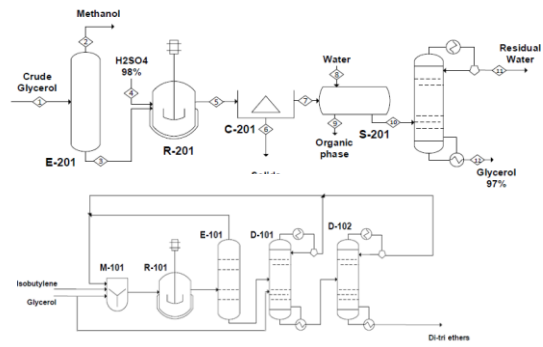
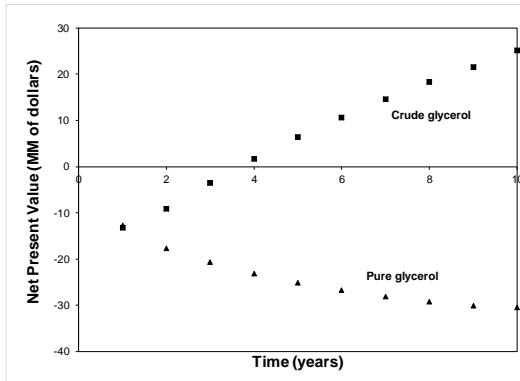
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Highlights

- Production of tert-butyl ethers of glycerol by etherification with isobutylene.
- The production cost is evaluated in Colombian context using different configuration.
- Techno-economic assessment to evaluate the most promising configuration.
- The production prices varied from 0.8 to 1.38 USD/kg for processes considered.
- Refining crude glycerol and a mixture of C₄ and isobutylene as raw materials.

Graphical Abstract



Answer to Reviewer 2

The study presents the research results on 'RAW GLYCEROL RE-VALUING THROUGH ETHERIFICATION WITH ISOBUTYLENE: PROCESS DESIGN AND TECHNO-ECONOMICAL ASSESSMENT'. The originality of this manuscript should be emphasized more and this manuscript cannot be acceptable in its present form. Please consider the following comments and suggestion for further revision..

Answer

The authors thank the reviewer of the manuscript for the comments. These will help us to increase the quality of the paper. Below, we answer the specific comments of the reviewer:

Comment

A concise abstract is required. Also, more specific descriptions of authors' finding should be added in the abstract rather than overall result of study. The abstract should state briefly the purpose of the research, the principal results and major conclusions.

Answer

The abstract has been rewritten following the suggestions of the reviewer.

Comment

There are many research results about process design and assessment about value-added glycerol for the utilization of a renewable resource. What is the main advantages of this research? Please provide the advantage of these processes and compare to other recent

research papers. Please provide the novelty of this study and compare to other recent research papers in the view of technical and economical points.

Answer

Thank you for your recommendation. The advantage/contribution of this work is related to consider different sources of raw materials (C₄ fraction and crude glycerol) and their corresponding combination of scenarios in function of feed, since in the tert-butyl ethers of glycerol, the raw materials represents the highest percentage on the final product cost and economic feasibility. Also, the effect of isobutylene:glycerol molar ratio on techno-economical assessment and cost of product is studied. These studies have not been presented so far. Another aspect to consider is the case is carried out to real context of Colombian, which aims to explore a possibility of producing this kind of compounds (these are not produced or sold in Colombia) in local industry from byproduct generated by Biodiesel industry. Some text has been included in the abstract and in the introduction section to highlight the novelty of this work.

Comment

The explanation of results and discussion are not enough in '3.6. Production cost' and '3.7. Return of investment'. Authors need to provide more detailed explanations and discussions. Regarding the results, it is necessary to present the comparison data with the recent research results related the process design/assessment together with the relevant references.

Answer

Thank you for your recommendation. Some text has been included in these sections to extend the discussion and the most relevant references have been referred to.

Comment

Authors should discuss the potential industrial application of this technology in an economical and technical viewpoint.

Answer

Thank you for your recommendation. These aspects have been explained along the paper.

From the technical viewpoint the main results were obtained from sensitivity test (section 3.2 and 3.3):

- i) Reaction zone: the optimal values for reaction temperature and residence time were established.
- ii) Extraction zone: the optimal values glycerol flow for removing impurities from the raffinate phase were established.
- iii) Distillation operation: the optimal values for molar reflux ratio in distillation columns were established.
- iv) Figure 10 shows the total energy requirement for all scenarios and your relation with the operation units (section 3.4).

From economical viewpoint the main results are presented when compared the production cost and return of investment for different scenarios (section 3.6, 3.7, and 3.9). Some text has been included in the results and discussion section in order to highlight the most relevant results.

Comment

There are many figures and tables. Only major results should be included in the MS and the others should be described in supplementary data.

Answer

Thank you for your recommendation, the main information and relevant results have been included in the manuscript (Tables 1-5, Figures 1-5) and the others have been presented in supplementary data (Tables 1S-9S, Figures 1S-9S).

Thank you very much for your comments

Answer to Reviewer 5

This manuscript is focused on the etherification process of isobutylene or a mixture of C4 hydrocarbons with a high content of isobutylene with glycerol with the aim of producing a triglyceride adequate for the formulation of oxygenated additives for fuels. This is a nice strategy to reduce the surplus of glycerol in the market due to the increasing production of biodiesel. The authors focused in the process design and technoeconomical evaluation of the process based their calculations in experimental data from other authors, as this is a well-studied process. The paper is well-written and it can be read with pleasure.

Answer

The authors thank the reviewer of the manuscript for the comments. These will help us to increase the quality of the paper. Below, we answer the specific comments of the reviewer:

Comment

From the formal aspect, the authors should consider if they can reduce the number of tables and figures, which seems excessive, and create a supplementary material section, with the main information being include in the text of the manuscript.

Answer

Thank you for your recommendation, the main information and relevant results have been included in the manuscript (Tables 1-5, Figures 1-5) and the others have been presented in supplementary data (Tables 1S-9S, Figures 1S-9S).

Comment

Considering the content of the paper, there are several questions that remain unknown or not considered in the process design and, consequently, in the economic evaluation:

The catalysts that are usual in this process are Brönsted acids supported in resins or in clays. They undergo notable deactivation and, consequently, should be reactivated, with the subsequent impact in the process economy.

Answer

Authors do not deal with deactivation which influence is not possible to ignore. However, the R-Yield Aspen Plus module used to simulate the reaction in Aspen Plus does not allow us to consider the effect of catalyst. For this reason, we increased the price of glycerol some cents of dollar (0.02 USD / Kg of glycerol) to consider its possible effect in the process economy assuming that the raw material cost represents more than 88% of the total price in scenarios (see Table 2).

Comment

The authors have used a kinetic model that only reflects the main reactions, the etherification reactions, but not the side reactions of isobutylene (oligomer formation). Obviously, this reflects in a reduction in the number of operation units and streams in the flowsheet and improves the economy of the process in an artificial way, deviating from the more real situation.

Answer

Thank you for your observation. As the reviewer points out secondary reactions are present reducing the yield towards ethers and, therefore, the economy of process. However, in this work, we considered the use of the simplified kinetic model of glycerol etherification by isobutylene regarding only main reactions leading to ethers formation [18], since, the use of homogeneous catalyst, such p-toluenesulfonic acid gave the best performance and suppressed butylene dimerization to the low level [12, 17]. This text has been now included in the design process section on page 8 for clarification, as follows:

“This was performed using the simplified kinetic model of glycerol etherification by isobutylene regarding only main reactions leading to ethers formation as proposed by Berh and Obendorf [18], which consider the use of homogeneous catalyst, p-toluenesulfonic acid, since it gives the highest conversion and yield values in the reaction and suppresses butylene dimerization to the low level [12, 17]”

And some the text was modified:

“and p-toluensulfonic acid to speed up the process [12, 17]” on page 4.

“using p-toluensulfonic acid as catalyst were [20]:” on page 6

Comment

It is not evident in all the paper if the authors are using crude or pure glycerol. This is not clearly indicated in the description of the scenarios and appears as a possible solution to increase the economy of the process at the end of the manuscript.

Answer

One of objective of this work was study the possibility of use crude glycerol, since no work in this field of simulation integrated the crude glycerol. The first step of this work evaluated pure glycerol to later consider the crude glycerol. This idea is presented in the goal of work and more specifically in the raw materials section on page 6.

Comment

Finally, it is difficult to discern if the paper introduces new information in a field that, as I commented before, is well studied. In particular, the authors should emphasize the novelty of their findings if they compared them to the works by Liu and coworkers that are cited in this manuscript. In particular, they should consider what they add different from what is contained in:

Jingjun Liu, Prodromos Daoutidis, Bolun Yang,

Process design and optimization for etherification of glycerol with isobutene,

Chemical Engineering Science,

Volume 144,

2016,

Pages 326-335,

ISSN 0009-2509,

<https://doi.org/10.1016/j.ces.2016.01.055>.

(<http://www.sciencedirect.com/science/article/pii/S0009250916300355>)

Answer

Thanks for your recommendation. The main contribution of this work is related to consider different sources of raw materials (C4 fraction and crude glycerol) and their corresponding combination of scenarios in function of feed, since in the tert-butyl ethers of glycerol, the raw materials represents the highest percentage on the final product cost and economic feasibility. Also, the effect of isobutylene:glycerol molar ratio on technological assessment and cost of product was studied. These studies have not been presented so far. Another aspect to consider is the case is carried out to real context of Colombian, which aims to explore a possibility of produce this kind of compounds (these are not produced or sold in Colombia) in local industry from byproduct generated by Biodiesel industry. Some text has been included in the abstract and introduction section to highlight the novelty of this work.

With respect to the works reported by Liu and coworkers, the differences have been commented in introduction and results and discussion sections.

Thank you very much for your comments

Answer to Reviewer 11

The manuscript was researched the price of DGTBE and TGTBE, Using C4 fraction as a source of isobutylene makes production costs higher because more raw materials have to be bought, but allows the formation of a gas mixture byproduct which helps the process revenue. The manuscript is suitable to public in this journal. However, some question should be solved.

Answer

The authors thank the reviewer of the manuscript for the comments. These will help us to increase the quality of the paper. Below, we answer the specific comments of the reviewer:

Comment

Some picture was lacked the scale of Y-axis, such as Figure 10, Figure 11,

Answer

These Figures have been improved following the indications of the reviewer (Figure 2 and 3, in the new nomenclature).

Comment

Some Figure should be amended for improving quality of Figure.

Answer

Figures have been revised in order to improve their quality.

Comment

Some literature is relevant to this article, like reference : Journal of Alloys and Compounds 720 (2017) 360-368 ; Journal of the Taiwan Institute of Chemical Engineers 87 (2018) 131-139. These literature should be added in the references.

Answer

Thanks for your recommendation. These references have been included in the manuscript (new references 7 and 8).

Thank you very much for your comments.

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4 **RAW GLYCEROL RE-VALUING THROUGH ETHERIFICATION WITH**
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6 **ISOBUTYLENE: PROCESS DESIGN AND TECHNO-ECONOMICAL**
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8 **ASSESSMENT**
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59 Suarez).
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4 **ABSTRACT:**
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7 This study evaluates the techno-economic feasibility to produce tert-butyl ethers of
8 glycerol in Colombia using glycerol obtained from biodiesel production. The major
9 drawback of this process is related to the high costs associated to the isobutylene
10 reagent used for this reaction. Three possible scenarios, using isobutylene:
11 glycerol molar ratios of 2:1 and 4:1, have been evaluated by simulation and
12 techno-economical assessment using pure isobutylene, C₄ fraction and a mixture
13 of C₄ and isobutylene as well as a refining stage for crude glycerol. The desired
14 product, a mixture of di- and tri- ethers of glycerol (h-GTBE) was obtained in high
15 amounts for the three scenarios (92 - 99 wt %) and a direct relation between
16 production cost and raw material cost was established. The prices for h-GTBE
17 were higher than the proposed selling prices; however, the formation of byproduct
18 (C₄ fraction) can make the process competitive. h-GTBE production did not have a
19 competitive price for any scenario at high isobutylene: glycerol molar ratio. The
20 production price was lowered by around 20% for all scenarios when crude glycerol
21 was considered. Finally, competitive price of h-GTBE (0.96 \$/kg) and NPV positive
22 was obtained using a mixture of C₄ and isobutylene and crude glycerol.
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50 **Keywords:** Tert-butyl ethers of glycerol (h-GTBE); process simulation; techno-
51 economical assessment; glycerol; isobutylene.
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1. INTRODUCTION

Alternative sources of renewable fuels have become relevant during the last decade in Colombia due to shortage of oil sources and their negative impact over the environment. Biodiesel production is a sustainable option that has been widely implemented worldwide. In 2017, 460 kilotons of biodiesel were produced in Colombia [1]. Glycerol is the main byproduct of biodiesel production by roughly 10% in weight, but it is obtained with impurities such as soaps, free fatty acids (FFA), unreacted raw materials, catalyst (commonly sodium hydroxide) and small amounts of biodiesel [2]. Due to the increase of glycerol production from biodiesel, its price has considerably decreased. To solve this problem, it appears necessary the conversion of glycerol into high added-value products.

Glycerol is a versatile raw material that can be used in different markets such as textile industry to produce 1,3-propanediol [3-4], food industry where it is used as sweetener and solvent, and pharmaceutical industry to produce soaps, ointments, shaving creams and several other personal care products [5] and butanol–ethanol [6]. Another pathway for glycerol conversion is the production of glycerol carbonate with interesting applications in novel solvents, carries in batteries, cosmetics and monomer for polymers. The viability using solid catalysts have been studied by Wu et al, showing high values in conversion and selectivity [7-8].

Glycerol can be also used to produce tert-butyl ethers of glycerol (h-GTBE) through etherification with isobutylene (IB) or tert-butyl alcohol (TBA). h-GTBE is a potential fuel-additive due to its high oxygen content and can potentially reduce both carbon monoxide and particulate matter emissions [9-11]. Additionally, these high tert-

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4 butyl ethers can also diminish the usage of traditional fuel additives that are
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6 harmful to the environment due to their low biodegradability and petrochemical
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8 origin, such as methyl-tert-butyl ethers and ethyl-tert-butyl ethers [12].
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12 Tert-butylation of glycerol is usually carried out with tert-butyl alcohol, however, the
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14 usage of isobutylene has gained relevance due to higher conversion of glycerol
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16 and higher selectivity to the desired products, DGTBE (glycerol tert-butyl di-ethers)
17
18 and TGTBE (glycerol tert-butyl tri-ethers) [13-18]. High pressures are required to
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20 keep isobutylene in liquid phase and acid catalysts such as Amberlyst-15,
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22 Amberlyst-35 and p-toluensulfonic acid to speed up the process [14, 19]. Three
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24 main processes have been proposed for the production of DGTBE and TGTBE (h-
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26 GTBE) with isobutylene [20-22].
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33 Behr and Obendorf designed a process where three chained reactors were used in
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35 cascade with an extraction column, a flash evaporator and a rectifying column [20].
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37 Top products were DGTBE and TGTBE while bottom products were glycerol and
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39 MGTBE (mono glycerol tert-butyl ether), which were subsequently recycled to the
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41 reactors, allowing an almost full conversion of glycerol. The process designed by
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43 Di Serio et al. had a similar reaction zone to that proposed by Behr and Obendorf,
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45 but employed an extraction column using biodiesel as solvent, where top product
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47 went to a flash evaporator to separate glycerol and MGTBE from fatty acids, and
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49 bottom product was a mix of biodiesel and high glycerol ethers [21]. The process
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51 proposed by Behr and Obendorf has been applied to others studies [19, 23, 24].
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57 Martín and Grossmann considered the production of biodiesel with tert-butyl ethers
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4 of glycerol and found that the production of ethers increased the cost of the
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6 biofuels by a factor of 3 due to price of isobutylene [19].
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10 Finally, in the process designed by Liu et al [22], the reaction kinetics took into
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12 account isomerization of isobutylene, which is an undesired product, slowing
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14 DGTBE and TGTBE production. Two extraction towers and two distillation columns
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16 were used to isolate isobutylene dimers (DIB), obtaining DGTBE and TGTBE as
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18 bottom product of the second distillation column and DIB as side outlet [22].
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20 Although each of these processes obtain a high purity product, the first two do not
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22 take into account the production price, subsequent studies do not show evaluation
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24 of economic feasibility and the last one is not feasible due to high prices of raw
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26 materials, especially because of the cost of pure isobutylene. None of these works
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28 considered the use of crude glycerol as raw material in the etherification route for
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30 glycerol conversion.
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37 The goal of this work is to analyze the feasibility of DGTBE and TGTBE production
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39 in Colombian context considering different sources of raw materials, pure
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41 isobutylene, C₄ fraction, and a mixture of C₄ fraction and pure isobutylene as well
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43 as glycerol obtained as byproduct from biodiesel process by simulation and
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45 techno-economical assessment. Three possible scenarios will be defined and
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47 studied. The process design and simulation will be done in Aspen Plus V9 and the
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49 techno-economic assessment in Aspen Economic Analyzer V9.
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2. PROCESS DESIGN

2.1. Raw Materials

The raw materials used were glycerol and isobutylene for scenario 1, glycerol and C₄ fraction for scenario 2, and glycerol and C₄ fraction enriched with isobutylene for scenario 3. C₄ fraction was a mixture of four carbon olefins obtained from catalytic cracking of oil [25] that contains roughly 20% of isobutylene [13]. In a second stage of analysis, the simulation was done using crude glycerol from biodiesel instead of pure glycerol including a purification step. Compositions for crude glycerol and C₄ fraction are reported in Tables 1S and 2S [14, 26]. The composition of the C₄ stream enriched with pure isobutylene is also shown in Table 2S (scenario 3).

2.2. Reaction process:

There are three consecutive reactions to be considered in this process (Figure 1S): etherification of glycerol with isobutylene to produce two MGTBE isomers; etherification of MGTBE with isobutylene to obtain two DGTBE isomers; finally, etherification of DGTBE with isobutylene to led TGTBE. These reactions occur in series and are reversible. They are usually produced using different acid catalysts. The reaction kinetics proposed by Behr and Obendorf using p-toluensulfonic acid as catalyst were [20]:

$$r_{MGTBE} = k_{MGTBE} \cdot C_G \cdot C_{IB} - k_{-MGTBE} \cdot C_{MGTBE} \quad (1)$$

$$r_{DGTBE} = k_{DGTBE} \cdot C_{MGTBE} \cdot C_{IB} - k_{-DGTBE} \cdot C_{DGTBE} \quad (2)$$

$$r_{TGTBE} = k_{TGTBE} \cdot C_{DGTBE} \cdot C_{IB} - k_{-TGTBE} \cdot C_{TGTBE} \quad (3)$$

Where r_i are reaction rates, k_i y k_{-i} are reaction constants and C_i is the molar concentration of component i . The differential equations that describe the concentration profile with respect to the time are:

$$\frac{dC_G}{dt} = -r_{MGTBE} \quad (4)$$

$$\frac{dC_{MGTBE}}{dt} = r_{MGTBE} - r_{DGTBE} \quad (5)$$

$$\frac{dC_{DGTBE}}{dt} = r_{TGTBE} - r_{TGTBE} \quad (6)$$

$$\frac{dC_{TGTBE}}{dt} = r_3 \quad (7)$$

$$\frac{dC_{IB}}{dt} = -r_1 - r_2 - r_3 \quad (8)$$

Where, $\frac{dC_i}{dt}$ is the change of concentration with respect to the time of specie i .

The reaction rate constant follows the Arrhenius law:

$$k_i = k_{0,i} \cdot \exp\left(-\frac{E_{A_i}}{R \cdot T}\right) \quad (9)$$

Where k_i is the reaction constant of specie i , $k_{0,i}$ is the pre-exponential factor, E_{A_i} is the activation energy of species i in $\frac{J}{mol}$, and R is the ideal gas constant in energy units ($R = 8.314 \frac{J}{molK}$). Table 3S shows pre-exponential and energy parameters obtained by Behr and Obendorf [20] that is going to be used to model the reaction zone in all cases.

2.3. Methodology: process simulation

The methodology was developed in three stages using different computational tools. The first stage consisted of the modelling of the reaction zone that generates the concentration profiles of reactants and products in function of time. This was performed using the simplified kinetic model of glycerol etherification by isobutylene regarding only main reactions leading to ethers formation as proposed by Berh and Obendorf [20], which consider the use of homogeneous catalyst, p-toluenesulfonic acid, since it gives the highest conversion and yield values in the reaction and suppresses butylene dimerization to the low level [14, 19]. A sensitivity test was used to determine the optimal temperature between 323 and 363 K, comparing glycerol conversion at each temperature. The second stage regards to process simulation was carried out in Aspen Plus V9 to obtain mass and energy balances. UNIFAC was chosen as the thermodynamic method for this stage, taking into account the lack of empiric data available for the complex liquid-liquid interactions between the several compounds present in the simulation. Last stage was the techno-economical assessment of the process, carried out in Aspen Process Economic Analyzer V9, where production cost of the product (in USD/kg), depreciation expenses, raw material total cost, utilities, energy cost, initial investment and Net Present Value (NPV) were determined. Production costs were calculated for a molar ratio of 1:2 and 1:4 for scenarios 1, 2 and 3 with pure glycerol.

2.4. Process description

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4 1.5 ton/h of glycerol was processed for each scenario corresponding to 27% of net
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6 annual production of glycerine in Colombia. The flowsheet of the Behr and
7
8 Obendorf process was used as base to building the flowsheet for the different
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10 scenarios proposed, which showed differences in function of the raw materials
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12 sources.
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15 16 17 **2.3.1. Scenario 1** 18

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20 Figure 1 shows the flowsheet when pure glycerol and isobutylene were considered
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22 as raw materials (scenario 1). The reactants were mixed (M-101) and taken to the
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24 reaction specifications (80 °C and 20 bar) by cooling and heating procedures.
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26 MGTBE, DGTBE and TGTBE were obtained, with a glycerol conversion of 92%.
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28 Extracting and recycling MGTBE is suitable to increase its conversion into high
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30 ethers. The reaction products entered in an extraction column (E-101), where
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32 glycerol was used as solvent to extract the MGTBE. Two phases were produced:
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34 an aqueous phase, rich in MGTBE glycerol as extract, and an organic phase, rich
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36 in DGTBE and TGTBE as raffinate. The extract was recycled to the mixer (M-101).
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38 It is important to note that the glycerol used in this step was employed as raw
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40 material (half of the initial fed). The raffinate went through a distillation train (D-101
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42 and 102) where top product was unreacted glycerol and MGTBE, which was
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44 recycled to M-101 and bottom product was the desired mixture of DGTBE and
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46 TGTBE at 99% of purity.
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53 54 **2.3.2. Scenario 2** 55

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57 The process for scenario 2 is shown in Figure 2S. A mixture of C₄ and glycerol
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59 (half of the amount needed for the reaction) were mixed (M-101) and submitted to
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4 reaction conditions of 20 bar and 80 °C. It was assumed that glycerol only reacts
5 with isobutylene from C₄ fraction; other compounds present in C₄ fraction were
6 considered inert. The mixture obtained from reactor went through flash evaporator
7 (F-101) obtaining most of the C₄ olefins as top product. Bottom product was taken
8 to extraction column (E-101) with the rest of the glycerol feed as solvent. The
9 extract, rich in MGTBE and glycerol, was recycled to M-101 and the raffinate
10 underwent distillation (D-101). The top product was the remaining C₄ gases and
11 trace amounts, which were moved to mixer-102 along with F-101 top product. The
12 bottom product was the desired mix of DGTBE and TGTBE with 93%.
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26 **2.3.3. Scenario 3**

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28 The flowsheet for scenario 3 is displayed in Figure 3S which mainly reduced the
29 flow of inert components. For this purpose, the C₄ feed was decreased in a half
30 and a new stream with pure isobutylene was added to preserve the molar ratio.
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32 The process was similar to scenario 2 but a different stream entered in M-101.
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41 **2.3.4. Purification of raw glycerol**

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43 Raw glycerol was fed in an evaporator (E-201) at 20 °C and 1 bar where the
44 majority of the methanol was evaporated. The flow rich in glycerol was conducted
45 to reactor R-201 and sulfuric acid (98 wt/wt %) was used for neutralization reaction.
46
47 The products obtained were sodium salts and free fatty acids (FFA) together with
48 glycerol. The mixture was centrifuged to remove salts, proteins and ashes. The
49 stream, free from fatty acids, underwent to decantation, where an aqueous phase,
50 rich in glycerol and methanol, and an organic phase, rich in FFA were obtained.
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4 The aqueous phase was distilled obtaining water and the remaining methanol as
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6 top products, and glycerol 97 wt % as bottom product, as shown in Figure 4S.
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10 11 12 **3. RESULTS AND DISCUSSION** 13

14 15 **3.1. Global Mass Balance** 16

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18 Table 4S shows the mass flows (inlets and outlets) for the scenarios proposed
19 using pure glycerol. The molar ratio for scenario 2 was calculated taking into
20 account an isobutylene content of 20% wt/wt. A similar consideration was applied
21 for scenario 3, where an additional pure flow of isobutylene was fed. There were no
22 side products in scenario 1 since all unreacted glycerol and MGTBE were recycled.
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31 32 **3.2. Reaction Zone** 33

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35 A sensitivity test was made to determine the optimal reaction temperature,
36 between 323 and 363 K (Figure 5S) using a residence time of 400 min, as
37 proposed by several researchers for achieving the best glycerol conversion [13, 20,
38 27]. This test was developed varying temperature, which affects pre-exponential
39 values in the kinetic model (Arrhenius). As we can observe, at lower temperature,
40 conversion values did not reach equilibrium in the residence time considered. For
41 353 and 363 K, the chemical equilibrium was reached in 200 and 300 min,
42 respectively. After 300 min, the highest conversion of glycerol was obtained at 353
43 K. Therefore, 353 K was chosen as temperature to operate the reactor for all
44 scenarios.
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4 Figure 6S shows the concentration profile obtained from the solving of the
5 differential equation system from the mass balance proposed by Behr & Obendorf,
6 solved with Matlab using Runge Kutta's method. Glycerol was almost completely
7 converted into ethers after 200 min mainly resulting in MGTBE and DGTBE as
8 reaction products. However, the reaction should be kept at longer times (300 min)
9 to favour the conversion of MGTBE into DGTBE and TGTBE (see Figure 1S).

10
11 The R-Yield Aspen Plus module was used to simulate the reaction in Aspen Plus
12 (the effect of catalyst was not considered). The values of the yields obtained for
13 scenarios 1, 2 and 3 are presented in Table 5S. The highest product yield for each
14 scenario was obtained for DGTBE followed by MGTBE and TGTBE in this order.
15 These results are similar to those previously reported [20, 22]. The lower product
16 yield values observed for scenarios 2 and 3 can be explained by the presence of
17 inert gases in the C₄ feed, which was not present in scenario 1 where pure raw
18 materials were employed.

3.3. Separation Zone

3.3.1. Extraction Zone

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Liquid-liquid extraction was considered for separation of MGTBE, with the goal to
recycle it to the reaction zone and increase the production of DGTBE and TGTBE.
This step of separation was realized at atmospheric pressure and room
temperature (the reaction mixture was in liquid phase). Separation can be achieved
using glycerol as solvent because DGTBE and TGTBE are non-polar while
MGTBE and glycerol are polar compounds. A sensitivity test was carried out
varying the flow of glycerol fed to the extractor, between 100 and 600 kg/h (Figure

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4 **7S**). Low amounts of the desired compounds were detected in the extract flow at
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6 lower glycerol flow rates. However, the concentration of non-desired compounds in
7
8 the raffinate was higher. By increasing the glycerol flow rate up to 500 kg/h the
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10 goal of removing impurities from the raffinate was accomplished while keeping a
11
12 low flow of DGTBE and TGTBE in the extract.
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15 16 17 **3.3.2. Distillation Zone** 18

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20 For scenario 1, two distillations units were considered (Figure **1**) while one
21
22 distillation and one flash unit were applied for scenarios 2 and 3 (Figures **2S** and
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24 **3S**).
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28 The minimum molar reflux ratio, number of stages and feeding stage were
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30 obtained with the DSTWU module of Aspen Plus. The RadFrac module was used
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32 for simulation of distillation units. A sensitivity test varying the molar reflux ratio was
33
34 performed to lower the amount of DGTBE and TGTBE that leaves in the top
35
36 stream for each scenario. This objective was achieved with a molar reflux ratio of
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38 6.8, as shown in Figure **7S**. The total composition of the final product is indicated in
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40 Table **6S**. The final product purity was expressed as the sum of DGTBE and
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42 TGTBE fraction, which was 99% for scenario 1 and 92% for scenario 2 and 3.
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49 In scenario 1 the process considers two distillation units leaving trace amounts of
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51 glycerol and isobutylene and less than 0.5% of MGTBE as products. For scenario
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53 2 and 3, the purification process was significantly less effective, being the most
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55 abundant undesired products trans-2-butene and MGTBE, with 2.63 % and 2.22%
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57 for scenario 2, and 2.53 % and 2.23 % for scenario 3, respectively. Although the
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4 final product was less pure for scenarios 2 and 3, in which C₄ fraction was used,
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6 these compositions comes near to those reported by other authors [20, 27].
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10 The composition of the byproducts obtained for scenarios 2 and 3 is reported in
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12 Table 7S. Butane isomers were mainly present, being the most abundant trans-2-
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14 butene and 1-butene with more than 33 % for each, and trace amounts of MGTBE
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16 and DGTBE, less than 0.1%, for both cases.
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19 20 **3.4. Energy Consumption** 21

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23 Energy consumption was calculated by adding the absolute values of energy or
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25 work requirements for process equipment (Table 1). Negative or positive values
26
27 indicate if the unit operation requires withdrawn or added heat. The heat exchanger
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29 units were simulated with a shortcut method that does not require a service stream
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31 to be added, but for cost-calculation purposes, water and ethylene-glycol were
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33 chosen as cooling agents and water steam at low, medium and high pressure were
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35 chosen as heating agents.
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41 In the three scenarios, the major energy requirements were present in the reactor
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43 (R-101), (about of 2.8 MW for each scenario). The total condenser in distillation
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45 unit (D-101) had the second higher energy requirement with 1.62 MW for scenario
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47 1 and, the condenser (C-101) for scenarios 2 and 3, with -0.722 MW and -0.468
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49 MW, respectively.
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54 Figure 2 shows the total energy requirement for all scenarios. The scenario
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56 exhibited the highest energy consumption, followed by scenario 2 and 3, in this
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58 order. The difference between scenarios 2 and 3 was not significant since in
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4 scenario 3 the amount of raw materials was lower (about of 2 tons/h). This means
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6 that the 2 MW extra requirement for scenario 1 can be attributed to the usage of a
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8 second distillation tower.
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10 11 12 13 14 15 **3.5. Techno-Economical Assessment**

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18 The techno-economic assessment aims to calculate production costs and incomes
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20 by product sales. A comprehensive evaluation of different costs leads to the plant
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22 operating costs adapted to the Colombian parameters with a project lifetime of 10
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24 years; indicators such as internal return rate (IRR), industry taxes, water, fuel and
25
26 electricity prices, as well as wages were those typically used in Colombia [28]. Raw
27
28 material prices were taken from works reported by Liu and Salem [22, 27, 29].
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30 Table 8S shows the values used.
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36 It has been reported that DGTBE and TGTBE (h-GTBE) have excellent properties
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38 as fuel additives for biodiesel and gas, due to its high solubility and oxygen content
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40 [12], but it is not currently sold or produced in Colombian, making difficult to
41
42 determine a selling price. For simulation purposes, the price of methyl-tertbutyl-
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44 ether, which is a fuel additive being currently produced and sold in Colombia was
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46 used.
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51 Since for scenarios 2 and 3, significant amounts of by-products were obtained,
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53 mainly 1-butene, trans and cis 2-butene, it is proposed that the mixture can be
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55 commercialized (used as cooling agent and/or industrial fuel). A selling price was
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4 assigned to this mixture using LPG as reference for price and simulation purposes
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6 [30].
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9 10 **3.6. Production cost**

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12 The production cost was calculated adding up the prices associated to raw
13 materials, total utility costs, depreciation expenses, operating labour cost,
14 maintenance cost, operating charges, plant overhead, and general and
15 administrative cost and divided by the total mass flow of the product in the 8304
16 hours of production period (Table 2).
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25 Regarding scenario 1, the raw material cost represents the highest production
26 expense, approximately 88% of the total price, followed by general and
27 administrative cost at 7% and depreciation expenses with 5%. This distribution was
28 similar for scenarios 2 and 3. This is remarkable since in the majority of industrial
29 processes (and these specifically), raw materials represents approximately more
30 than 50% of the total production costs [31].
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41 The production costs for the desired product and the gas mixture byproduct are
42 reported in Table 3. The lowest production cost of the h-GTBE obtained in scenario
43 1 (1.02 USD/kg) was close to the selling price of MTBE (1.1 USD/kg, Table 8S).
44 The production price was higher for scenarios 2 and 3 because there was a higher
45 raw material mass flow. A direct relation between production cost and raw material
46 cost can be established. This price is mainly affected by the high cost of pure
47 isobutylene, which is 1.6 USD/kg. C₄ fraction has much lower price (0.46 USD/kg),
48 however, it has only 20 % wt/wt of isobutylene, therefore, it is necessary to feed 5
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4 times for keeping the molar ratio. In addition, byproducts can be obtained using C₄
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6 fraction.

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10 The prices of byproduct (from C₄ fraction) obtained for scenarios 2 and 3 were
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12 0.838 and 1.48 USD/kg, respectively. This difference is due to the amount of C₄
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14 fed. The byproduct in scenario 2 has a promising production price since it is lower
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16 than its reported price (LPG; Table 8S). **The integrated approach of a multiproduct**
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18 **portfolio leads to reductions in costs.**

21 22 **3.7. Net Present Value**

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25 The return of investment and the time required for recovering total capital cost
26
27 invested in the project **were studied by Net Present Value (NPV), as shown in**
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29 **Figure 3 for all scenarios. Net Present Value (NPV) behaviour illustrates the**
30
31 **economic potential and risk of commercialization of the processes studied. By**
32
33 **comparing their NPVs, the most favorable process conditions for the**
34
35 **commercialization of product can be determined. The process is profitable when**
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37 **the NPV is greater than zero (NPV > 0) [32].** For scenario 1, the results shown that
38
39 it is not feasible since the Net Present Value (NPV) was negative after 10 years of
40
41 project lifetime, which means that the equilibrium point never was reached, and
42
43 investment was not recovered. This behaviour is due to the non-competitive
44
45 production price since there was no significant difference between production price
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47 and selling price (1.02 vs 1.15 USD/kg), for a relevant revenue to be obtained.
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49 However, for scenarios 2 and 3 the equilibrium was reached after the first year.
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4 The prices for h-GTBE were higher than the proposed selling prices, however, the
5 formation of byproduct in scenarios 2 and 3 can make the process competitive,
6 while, the high cost of pure isobutylene affects it negatively (scenario 1). Therefore,
7 the use of C₄ is a good alternative. Others possibilities such as producing
8 isobutylene from a glucose source [19] or refining crude glycerol from biodiesel
9 production [32] will make scenario 1 a competitive process.
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25 **3.8 Isobutylene:glycerol molar ratio**

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28 Several works suggested that the use of a high isobutylene: glycerol molar ratio
29 increased the glycerol conversion and resulted in a higher selectivity towards h-
30 GTBE [9, 13, 22]. However, these studies did not take into account the production
31 price for an industrial scale process.
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39 In this work, techno-economical assessment was done for all scenarios at high
40 isobutylene:glycerol molar ratio (4:1). The flow of isobutylene was 3782.5 kg/h for
41 scenario 1, 11158 kg/h of C₄ fraction for scenario 2, and 5579 and 1891.25 kg/h for
42 C₄, and isobutylene, respectively for scenario 3. As we can see in Figure 9S, a
43 total glycerol conversion was achieved and TGTBE selectivity increased. The
44 amount of unreacted isobutylene increased, 2 mole of isobutylene/l for a molar
45 ratio 2:1 (Figure 6S) to 9 mole of isobutylene/l for a molar ratio of 4:1 (Figure 9S).
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57 The final product presented a purity of 99% for all cases but the increase of the raw
58 materials flow rate increased the production cost, as shown in Table 4. h-GTBE
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4 production did not have a competitive price for any scenario at high
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6 isobutylene:glycerol molar ratio. The byproduct (LPG) price decreased greatly,
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8 reaching prices of 0.71 and 0.94 \$/kg, respectively, because there is much more
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10 C₄ fraction being fed.
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14 Figure 4 shows that the return of investment was reached for scenarios 2 and 3
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16 after 2 years of project lifetime. However, this cannot be attributed to the main
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18 product, since its production price was higher than its selling price. Reaching a
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20 return of investment only was possible because the production price of the gases
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22 was much cheaper now and had a major profit.
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26 27 **3.9 Crude raw glycerol** 28 29

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31 An alternative for lowering the costs could be the purchase of crude raw glycerol.
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33 This way will consider refine crude raw glycerol obtained from biodiesel industry.
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35 This glycerol has low commercial price and is generally considered waste due to
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37 the high concentration of biodiesel production residues, such as methanol, FFA,
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39 soap, water, basic catalyst and biodiesel that it has [33]. With the goal to decrease,
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41 the price of production, it is considered to use the raw glycerol obtained from
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43 biodiesel industry as raw material for h-GTBE production.
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48 The mass flow of crude glycerol selected was 2.72 ton/h. This flow was calculated
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50 with the goal to obtain 1.5 ton/h of purified glycerol after the refining process was
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52 completed. Global mass balance for the refining process is shown in Table 9S;
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54 streams are named according to the flowsheet presented in Figure 1S. The
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4 simulation of purification process allowed us to obtain 1.55 ton/h of glycerol with a
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6 purity of 95.6% and 290 kg/h of methanol.
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10 Techno-economical assessment was made considering that crude glycerol from
11
12 biodiesel is a waste material that does not have commercial value. Additionally,
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14 methanol was taken as an additional byproduct, because it can be recycled to the
15
16 biodiesel production plant, lowering the raw material prices. Table 5 shows the
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18 production prices when the glycerol refining process was added to the simulation
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20 for all scenarios.
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25 The production price was lowered by around 20% for all scenarios; the raw
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27 material cost per period was lowered by around 5 million dollars. This is about 19
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29 to 22% of total cost per period for all the scenarios studied. This can be explained
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31 by the price associated to the purchase of pure glycerol. The reduction of the
32
33 production price of h-GTBE made the scenario 1 feasible, with return of investment
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35 after 4 years of project lifetime. Figure 5 shows a comparison with pure and crude
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37 glycerol for scenario 1.
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43 Scenario 1 showed the lowest overall production price and the investment price
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45 was recovered after half of the projects lifetime. It is considered, then, that it is
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47 possible to improve the projects feasibility and profitability. Scenario 2 still has a
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49 non-competitive production price (just 14 cents below selling price) and the
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51 revenue is mostly attributed to the production of LGP.
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56 Scenario 3 is considered the best possible scenario, because it has competitive
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58 production prices for the main product and byproduct (0.96 and 1.17 \$/kg,
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4 respectively) and also has the less energy consumption and the lowest capital cost
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6 investment.

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10 The results obtained considering different alternatives of raw material sources for
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12 tert-butyl ethers of glycerol production allowed us to confirm that the raw materials
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14 represents the highest percentage on the final product cost as previously reported
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16 by other authors [19, 22]. From the technical viewpoint the flowsheet proposed for
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18 the three scenarios in function of raw materials resulted in high conversion and
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20 yield values. From the techno-economic point of view, the production of tert-butyl
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22 ethers of glycerol was feasible when crude glycerol and mixture of C₄ fraction and
23
24 pure isobutylene were considered. The cost of h-GTBE was lower than that
25
26 reported by Liu et al [22] using glycerol and pure isobutene (0.96 vs 1.201 \$/kg,
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28 respectively).

29 30 31 32 33 34 35 **CONCLUSIONS**

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38 The production cost has been mainly related to the high raw material prices,
39
40 specifically pure isobutylene for the three study cases. Using a higher
41
42 isobutylene:glycerol molar ratio to increase the selectivity of DGTBE and TGTBE
43
44 (h-GTBE) resulted in higher production costs that make all cases unfeasible. Using
45
46 C₄ fraction as a source of isobutylene makes production costs higher because
47
48 more raw materials have to be bought, but allows the formation of a gas mixture
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50 byproduct which helps the process revenue. It is preferred to implement a process
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52 that uses a combination of C₄ and pure isobutylene. Selling the residual gases as a
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54 byproduct, allowed scenarios 2 and 3 to be feasible with pure glycerol despite the
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56 non-competitive production price of h-GTBE, with a return of investment after 2
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years of project's lifetime, respectively. The production of glycerol tert-butyl ethers through etherification with isobutylene is viable in Colombian soil if raw material prices are reduced. Adding a purification stage for crude glycerol, lowers the production price in 20% for all cases, allowing a return of investment after 4 years for the worst case and after 1 year for the best case. Scenario 3 was the best overall case due to its lower capital cost, energy consumption and competitive production prices for the main product and byproduct.

REFERENCES

- [1] Federación Nacional de Combustibles, Producción de Biodiesel. <http://www.fedebiocombustibles.com/estadistica-produccion-titulo-Biodiesel.htm>, 2018 (accessed 9 May 2018).
- [2] F. Yang, M. A. Hanna, R. Sun, Value-added uses for crude glycerol--a byproduct of biodiesel production, *Biotechnol Biofuels* 5 (2012) 13. <https://doi.org/10.1186/1754-6834-5-13>.
- [3] A. Hiremath, M. Kannabiran, V. Rangaswamy, (2011). 1,3-Propanediol production from crude glycerol from jatropha biodiesel process. *New Biotechnol.*, 28(1) (2011) 19–23. <https://doi.org/10.1016/J.NBT.2010.06.006>.
- [4] S. T. S Veras, P. Rojas, L. Florencio, M. T. Kato, J. L. Sanz, Production of 1, 3-propanediol from pure and crude glycerol using a UASB reactor with attached biomass in silicone support. *Bioresource technology*, 279 (2019), 140-148. <https://doi.org/10.1016/j.biortech.2019.01.125>.
- [5] H. W. Tan, A. R. Abdul Aziz, M. K. Aroua, M. K, Glycerol production and its applications as a raw material: A review, *Renew. Sustain. Energy Rev.* 27 (2013) 118–127. <https://doi.org/10.1016/J.RSER.2013.06.035>.
- [6] J. Lu, T. Chen, Y. Jiang, W. Zhang, W. Dong, W, J. Zhou, F. Xin, The draft genome sequence of *Clostridium* sp. strain CT7, an isolate capable of producing butanol but not acetone and 1, 3-propanediol from crude glycerol. *3 Biotech* (2019), 9(2), 63. <https://doi.org/10.1007/s13205-019-1598-7>.
- [7] Y. Wu, X. Song, F. Cai, G.Xiao, *Synthesis of glycerol carbonate from glycerol*

1
2
3
4 and diethyl carbonate over Ce-NiO catalyst: the role of multiphase Ni. *J. Alloy.*
5
6 *Compd* (720) (2017), 360-368. <https://doi.org/10.1016/j.jallcom.2017.05.292>
7
8

9
10 [8] Y. Wu, X. Song, J. Zhang, S. Li, X. Yang, H. Wang, G. Xiao, Synthesis of
11
12 glycerol carbonate from glycerol and diethyl carbonate over CeO₂-CdO catalyst:
13
14 the role of Ce⁴⁺ doped into CdO lattice. *J Taiwan Inst Chem Eng.* 87 (2018), 131-
15
16 139. <https://doi.org/10.1016/j.jtice.2018.03.023>
17
18

19
20 [9] J. Singh, J. Kumar, M. S. Negi, D. Bangwal, S. Kaul, M. O. Garg, Kinetics and
21
22 modeling study on etherification of glycerol using isobutylene by in situ production
23
24 from tert -butyl alcohol. *Ind. Eng. Chem. Res.* 54(19) (2015) 5213–5219.
25
26 <https://doi.org/10.1021/acs.iecr.5b00079>.
27
28

29
30 [10] F. Chang, Q. Zhou, S. X. Pan, Y. He, Catalytic upgrading of glycerol, a
31
32 promising biodiesel coproduct. In *Biomass, Biofuels, Biochemicals* (2020) (pp. 395-
33
34 405). Elsevier. <https://doi.org/10.1016/B978-0-444-64307-0.00015-9>
35
36

37
38 [11] Ö. D. Bozkurt, F. Yılmaz, N. Bağlar, S. Çelebi, A. Uzun, Compatibility of di-and
39
40 tri-tert-butyl glycerol ethers with gasoline. *Fuel* (2019), 255, 115767.
41
42 <https://doi.org/10.1016/j.fuel.2019.115767>
43
44

45
46 [12] S. Shanmuganathan, D. Natalia, A. van den Wittenboer, C. Kohlmann, L.
47
48 Greiner, P. Domínguez de María, Enzyme-catalyzed C–C bond formation using 2-
49
50 methyltetrahydrofuran (2-MTHF) as (co)solvent: efficient and bio-based alternative
51
52 to DMSO and MTBE. *Green Chem.* 12 (2010) 2240-2245.
53
54 <https://doi.org/10.1039/c0gc00590h>.
55
56

57
58
59 [13] K. Klepáčová, D. Mravec, A. Kaszonyi, M. Bajus, Etherification of glycerol and
60
61
62
63
64
65

1
2
3
4 ethylene glycol by isobutylene. Appl. Catal. A: Gen. 328 (2007) 1-13.

5
6 <https://doi.org/10.1016/j.apcata.2007.03.031>

7
8
9
10 [14] [A. Turan](#), [M. Hrivnák](#), [K. Klepáčová](#), [A. Kaszonyi](#), D. Mravec, Catalytic
11 etherification of bioglycerol with C4 fraction, Appl. Catal. A. Gen. 468 (2013) 313-
12 321. <https://doi.org/10.1016/j.apcata.2013.09.007>.
13
14

15
16
17 [15] M. D. González, Y. Cesteros, J. Llorca, P. Salagre, Boosted selectivity toward
18 high glycerol tertiary butyl ethers by microwave-assisted sulfonic acid-
19 functionalization of SBA-15 and beta zeolite, J. Catal. 290 (2012) 202-209.
20
21 <https://doi.org/10.1016/j.jcat.2012.03.019>.
22
23
24

25
26 [16] M. D. González, P. Salagre, E. Taboada, J. Llorca, E. Molins, Y. Cesteros,
27 Sulfonic acid-functionalized aerogels as high resistant to deactivation catalysts for
28 the etherification of glycerol with isobutene, Appl. Catal. B: Environ. 136-137
29 (2013) 287-293. <https://doi.org/10.1016/j.apcatb.2013.02.018>.
30
31
32

33
34 [17] M. D. González, P. Salagre, E. Taboada, J. Llorca, Y. Cesteros, Microwave-
35 assisted synthesis of sulfonic acid-functionalized microporous materials for the
36 catalytic etherification of glycerol with isobutene, Green Chem. 15 (2013) 2230-
37 2239. <https://doi.org/10.1039/C3GC40683K>.
38
39

40
41 [18] M. D. González, P. Salagre, M. Linares, R. García, D. Serrano, Y. Cesteros,
42 Effect of hierarchical porosity and fluorination on the catalytic properties of zeolite
43 Beta for glycerol etherification, Appl. Catal. A: Gen. 473 (2014) 75-82.
44
45 <https://doi.org/10.1016/j.apcata.2013.12.038>.
46
47
48

49
50 [19] M. Martín, I. E. Grossmann, Simultaneous optimization and heat integration for
51
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3
4 the coproduction of diesel substitutes: Biodiesel (FAME and FAEE) and glycerol
5
6 ethers from algae oil. *Ind. Eng. Chem. Res.*, 53(28) (2014) 11371–11383.
7
8 <https://doi.org/10.1021/ie402443t>.

9
10
11 [20] A. Behr, Arno, L. Obendorf, Development of a process for the acid-catalyzed
12
13 etherification of glycerine and isobutene forming glycerine tertiary butyl
14
15 ethers. *Eng. Life Sci.*2 (2002) 185–189. [https://doi.org/10.1002/1618-](https://doi.org/10.1002/1618-2863(20020709)2:7<185::AID-ELSC185>3.0.CO;2-4)
16
17 [2863\(20020709\)2:7<185::AID-ELSC185>3.0.CO;2-4](https://doi.org/10.1002/1618-2863(20020709)2:7<185::AID-ELSC185>3.0.CO;2-4).
18
19

20
21
22 [21] M. Di Serio, L. Casale, R. Tesser, E. Santacesaria, New Process for the
23
24 Production of Glycerol *tert* -Butyl Ethers, *Energy Fuels*, 24(9) (2010) 4668–4672.
25
26 <https://doi.org/10.1021/ef901230r>
27
28

29
30
31 [22] J. Liu, P. Daoutidis, B. Yang, Process design and optimization for etherification
32
33 of glycerol with isobutene. *Chem. Eng. Sci.*, 144 (2016) 326–335.
34
35 <https://doi.org/10.1016/j.ces.2016.01.055>
36
37

38
39 [23] E. Vlad, C.S. Bildea, G. Bozga, Robust Optimal Design of an Glycerol
40
41 Etherification Process. *Chem.Eng.Technol.*36 (2), (2013) 251–258.
42
43 <https://doi.org/10.1002/ceat.201200274>
44
45

46
47 [24] J.K . Cheng, C. L. Lee, Y.T Jhuang, J.D. Ward, I.L. Chien, Design and control
48
49 of the glycerol tertiary butyl ethers process for the utilization of a renewable
50
51 resource. *Ind. Eng. Chem. Res.* 50 (22), (2011), 12706–12716.
52
53 <https://doi.org/10.1021/ie2010516>
54
55

56
57 [25] Z. Qi, K. Sundmacher, E. Stein, A. Kienle, A. Kolah, Reactive separation of
58
59 isobutene from C₄ crack fractions by catalytic distillation processes, *Sep. Purif.*
60
61

1
2
3
4 Technol. 26(2–3) (2002) 147–163. [https://doi.org/10.1016/S1383-5866\(01\)00156-3](https://doi.org/10.1016/S1383-5866(01)00156-3)

5
6
7 [26] S. Hu, X. Luo, C. Wan, Y. Li, Characterization of crude glycerol from biodiesel
8 plants, J. Agric. Food Chem 60(23) (2012) 5915–5921.
9
10 <https://doi.org/10.1021/jf3008629>

11
12
13
14
15 [27] J. Liu, B. Yang, C. Yi, Kinetic Study of Glycerol Etherification with Isobutene.
16 Ind. Eng. Chem. Res. 52(10) (2013) 3742–3751. <https://doi.org/10.1021/ie400050v>

17
18
19
20 [28] J. A. Dávila, M. Rosenberg, C. A. Cardona. Techno-economic and
21 Environmental Assessment of p-Cymene and Pectin Production from Orange Peel,
22 *Waste Biomass Valori*. 6(2) (2015) 253–261. [https://doi.org/10.1007/s12649-014-](https://doi.org/10.1007/s12649-014-9339-y)
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99 [30] Global Petrol Prices. https://es.globalpetrolprices.com/lpg_prices/, 2018.
100 (accessed 9 May 2018).

101 [31] J. Moncada, M.M. El-Halwagi, C.A. Cardona, Techno-economic analysis for a
102 sugarcane biorefinery: Colombian case. *Bioresour. Technol.* 135 (2013) 533-543.
103 <https://doi.org/10.1016/j.biortech.2012.08.137>

104 [32] H. Wenhao, Q. Dang, M. Rover, R. C. Brown, M.M, Wright, Comparative
105 techno-economic analysis of advanced biofuels, biochemicals, and hydrocarbon
106 chemicals via the fast pyrolysis platform, *Biofuels*, 7(2016), 57-67,

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<https://doi.org/10.1080/17597269.2015.1118780>.

[33] M. Gupta, N. Kumar, Scope and opportunities of using glycerol as an energy source. *Renew. Sustain. Energy Rev.* 16(7) (2012) 4551–4556.

<https://doi.org/10.1016/j.rser.2012.04.001>.

[34] S. Veluturla, N. Archana, D. Subba Rao, N. Hezil, I. S. Indraja, S. Spoorthi, Catalytic valorization of raw glycerol derived from biodiesel: a review. *Biofuels*, 9(3) (2018) 305–314. <https://doi.org/10.1080/17597269.2016.1266234>

Table 1: Energy requirements for all scenarios (MW/h)

Unit	Scenario 1 (IB)	Scenario 2 (C ₄)	Scenario 3 (C ₄ -IB)
C-101	-0.255	-0.722	-0.468
P-101	-0.100	0.013	0.011
H-101	0.363	0.520	0.397
H-102	-0.167	-0.180	-0.132
H-103	-0.400	-0.078	-0.078
H-104	-	-0.060	-0.060
F-101	-	0.416	0.204
Cond. D-101	-1.626	-0.033	-0.033
Cond. D-102	-0.528	-	-
Reboiler D-101	-0.528	0.089	0.090
Reboiler D-102	0.529	0.000	0.000
Reactor R-101	2.799	2.772	2.778

Table 2: Cost of operation per year

Item	Scenario 1	Scenario 2	Scenario 3
USD (10 ³)	Cost/year	Cost/year	Cost/year
Raw Materials	20262.4	27666.8	24528.3
Total Utilities Cost	252.7	271.9	227.9
Depreciation Expenses	599.2	503.6	489.7
Operating Labor Cost	88.9	93.9	93.9
Maintenance Cost	33.3	26.4	23.6
Operating Charges	22.2	23.5	23.5
Plant Overhead	61.1	60.1	58.7
General and administrative Cost	1657.7	2251.4	1996.5
Total Cost	22977.6	30897.7	27442.0

Table 3: Production cost of desired products and gas mixture

Product	Cost (usd/kg)		
	Scenario 1	Scenario 2	Scenario 3
h-GTBE	1.020	1.380	1.230
LPG	-	0.838	1.480

Table 4: Production price of h-GTBE and LPG with isobutylene:glycerol molar ratio of 4:1

Product	Cost (\$/kg)		
	Scenario 1	Scenario 2	Scenario 3
h-GTBE	1.36	1.64	2.18
LPG	-	0.71	0.94

Table 5. Production costs with crude glycerol

Product	Cost (\$/kg)		
	Scenario 1	Scenario 2	Scenario 3
h-GTBE	0.801	1.086	0.962
LPG	-	0.670	1.170

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LEGENDS AND CAPTIONS

Figure 1. Flowsheet for tert-butyl ethers production (scenario 1).

Figure 2. Energy requirements for scenarios 1, 2 and 3.

Figure 3: Net Present Value for 10 years of project lifetime.

Figure 4: Return of Investment with isobutylene:glycerol molar ratio of 4:1

Figure 5. Scenario 1: NPV with pure and crude glycerol.

Supplementary Material

Table 1S. Composition of crude glycerol

Component	Composition (% w/w)
Glycerol	57.1
Methanol	11.3
Water	1.00
Soap	30.3
FAME	0.30
Glycerides	0.00
FFA	0.00
Ash	0.00

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Table 2S. Molar composition of C₄ fraction

Component	Scenario 2	Scenario 3
Propane	0.01	0.01
Propene	0.03	0.03
i-butane	0.56	0.047
n-butane	6.84	5.70
trans-2-butene	29.10	24.26
cis-2-butene	13.60	11.34
Isobutylene	20.65	34.43
1-butene	28.35	23.63
1,3-butadyene	0.09	0.07
others	0.09	0.08

Table 3S: Reaction parameters

Reaction	K_o	E_A [kJ/mol]
r_{MGTBE} ($\text{min}^{-1} \text{mol}^{-1}$)	3.04×10^8	74.04
$r_{-\text{MGTBE}}$ (min^{-1})	3.69×10^{13}	111.08
r_{DGTBE} ($\text{min}^{-1} \text{mol}^{-1}$)	1.70×10^{11}	92.80
$r_{-\text{DGTBE}}$ (min^{-1})	8.54×10^{14}	118.06
r_{TGTBE} ($\text{min}^{-1} \text{mol}^{-1}$)	2.26×10^{10}	92.56
$r_{-\text{TGTBE}}$ ($\text{min}^{-1} \text{mol}^{-1}$)	6.35×10^{15}	125.13

Table 4S: Global inlets and outlets in kg/h

Component	Scenario 1	Scenario 2	Scenario 3
Glycerol (in)	1552.2	1552.2	1552.2
Isobutylene (in)	1156.4	-	578.2
C ₄ (in)	-	5578.9	2789.5
DGTBE & TGTBE (out)	2708.6	2690.2	2692.3
Inert (out)	-	4440.9	2227.5

Table 5S: Yields of the Module (*R-Yield*)

Component	Scenario 1	Scenario 2	Scenario 3
Glycerol	0.0584	0.0131	0.0197
Isobutylene	0.1082	0.0145	0.0217
MGTBE	0.2763	0.0806	0.1209
DGTBE	0.4337	0.1636	0.2454
TGTBE	0.1234	0.0613	0.0920

Table 6S: Mass fraction of product desired.

Component (%)	Scenario 1	Scenario 2	Scenario 3
Propane	-	3.92×10^{-6}	3.96×10^{-6}
Propene	-	7.59×10^{-6}	7.66×10^{-6}
i-Butane	-	0.0135	1.34×10^{-2}
n-Butane	-	0.49	0.48
trans-2-butene	-	2.63	2.53
cis-2-butene	-	1.38	1.32
1-Butene	-	1.57	1.53
1,3-Butadiene	-	0.004	0.00
Glycerine	2.05×10^{-9}	0.28	0.28
Isobutylene	7.36×10^{-16}	0.16	0.32
MGTBE	0.39	2.22	2.23
DGTBE	73.53	63.20	63.20
TGTBE	26.08	28.04	28.09

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Table 7S: Mass fraction of byproducts.

Component (%)	Scenario 2	Scenario 3
Propane	0.0099	0.0099
Propene	0.0283	0.0284
i-Butane	0.7247	0.7144
n-Butane	8.6534	8.3446
trans-2-butene	35.1702	33.5854
cis-2-butene	16.3478	15.5328
1-Butene	34.8684	33.8494
1,3-Butadiene	0.0938	0.0912
Glycerine	0.0006	0.0006
Isobutylene	4.0203	7.7612
MGTBE	0.090	0.089
DGTBE	0.0132	0.0131
TGTBE	0.0607	0.0604

Table 8S: Raw materials, wages and services prices

Item	Value	Unit
Glycerol + catalyst	0.38	USD/kg
Isobutylene	1.60	USD/kg
C4	0.46	USD/kg
MTBE	1.15	USD/kg
LPG	0.65	USD/L
Industry Taxes	25.00	%
IRR	17.00	%
Operator	2.14	USD/h
Supervisor	4.29	USD/h
Electricity	0.10	USD/KWh
Water	1.25	USD/m ³
Fuel	7121	USD/MMBTU

Table 9S. Global mass balance for raw glycerol refining in kg/h

Stream	Mass Flow (kg/h)
1 (inlet)	2718.37
2 (outlet)	290.78
4 (inlet)	28.30
6 (outlet)	58.70
8 (inlet)	1500.00
9 (outlet)	847.31
11 (outlet)	1494.44
12 (outlet)	1555.43

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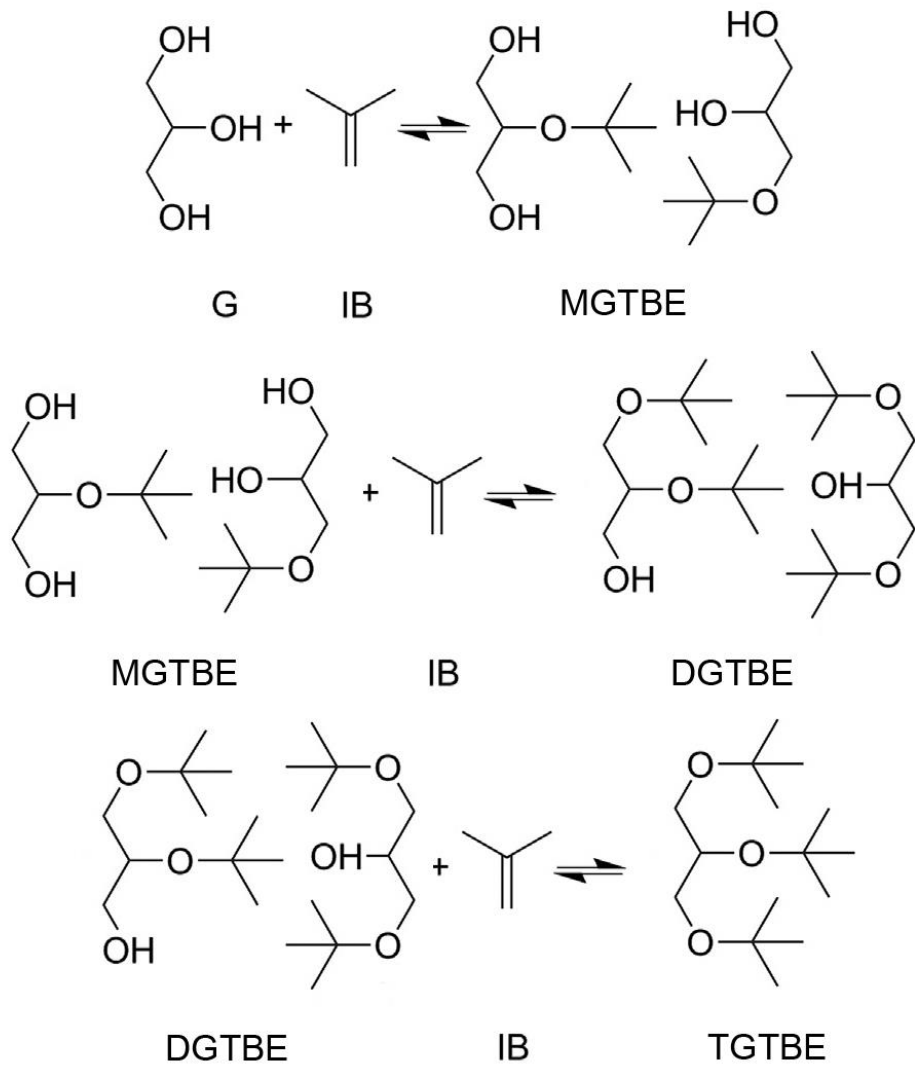


Figure 1S: Reaction scheme.

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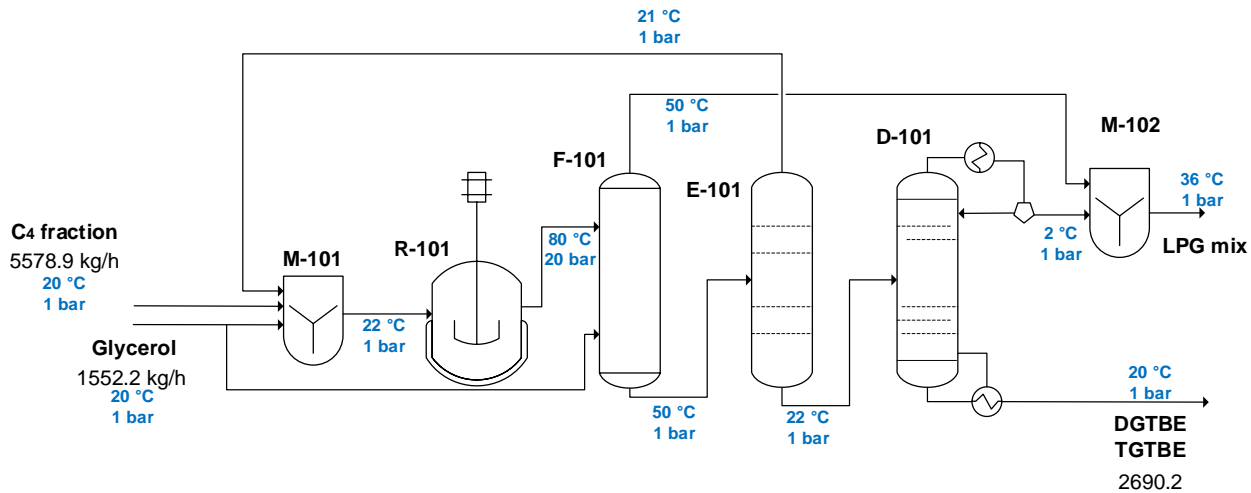


Figure 2S. Flowsheet for tert-butyl ethers production (scenario 2).

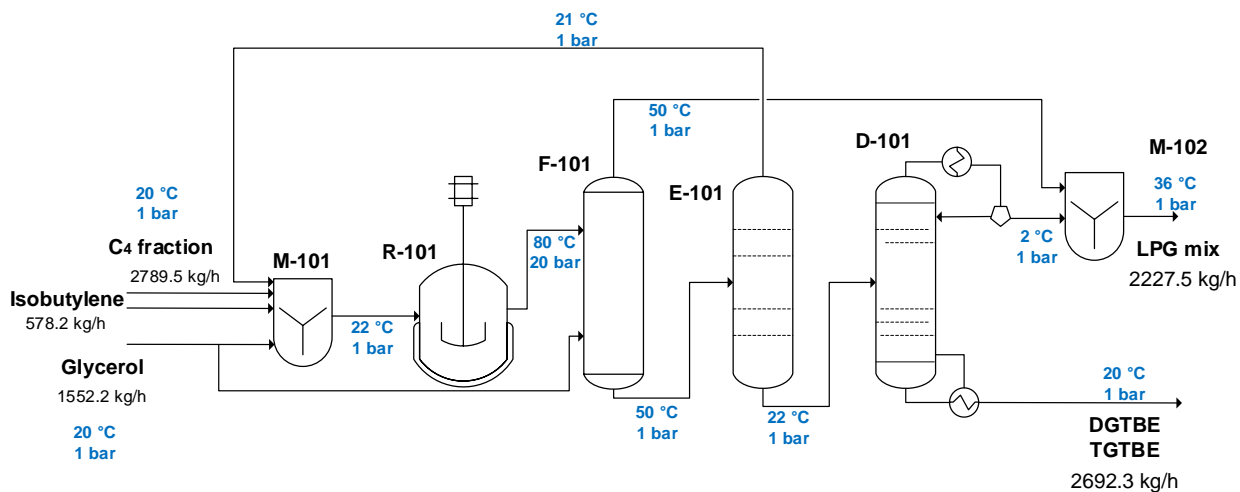


Figure 3S. Flowsheet for tert-butyl ethers production (scenario 3).

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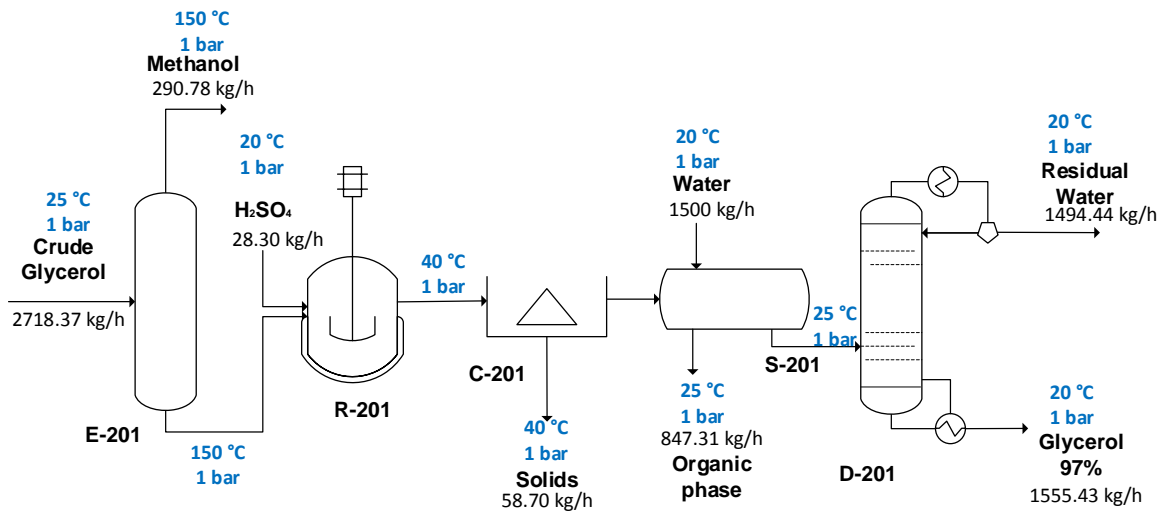


Figure 4S. Flowsheet for glycerol purification.

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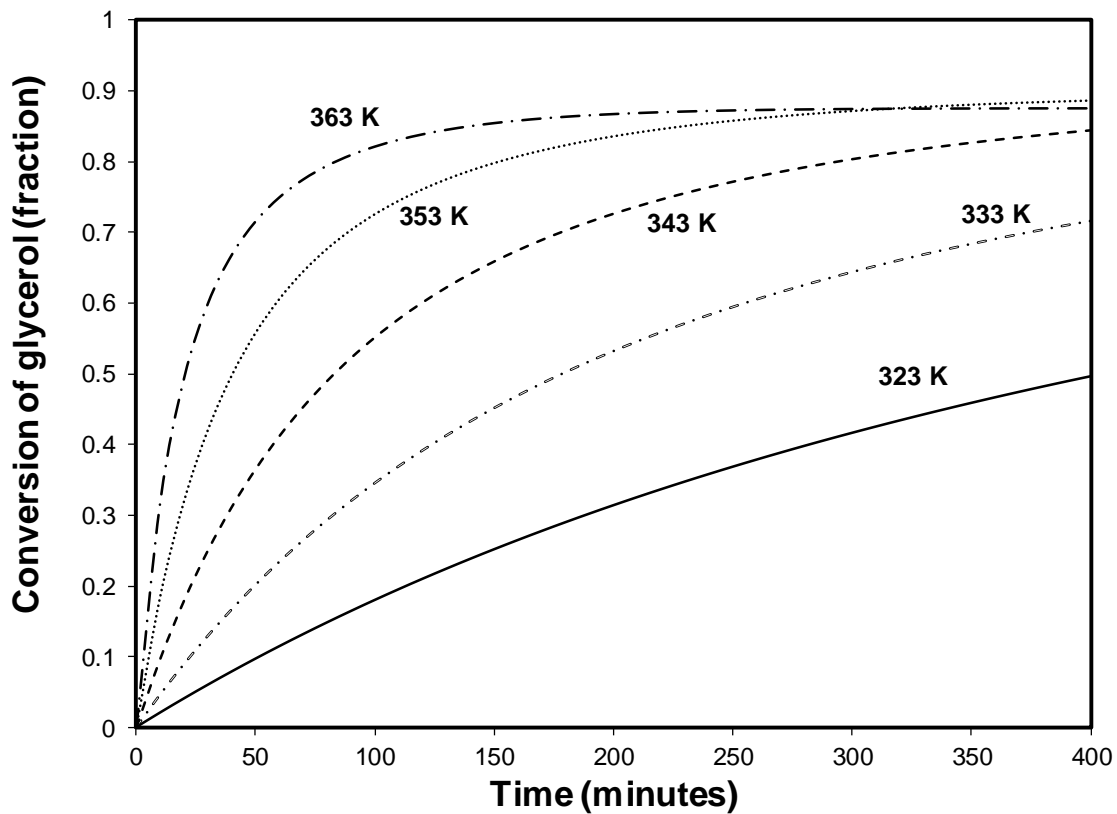


Figure 5S. Sensitivity test for glycerol conversion.

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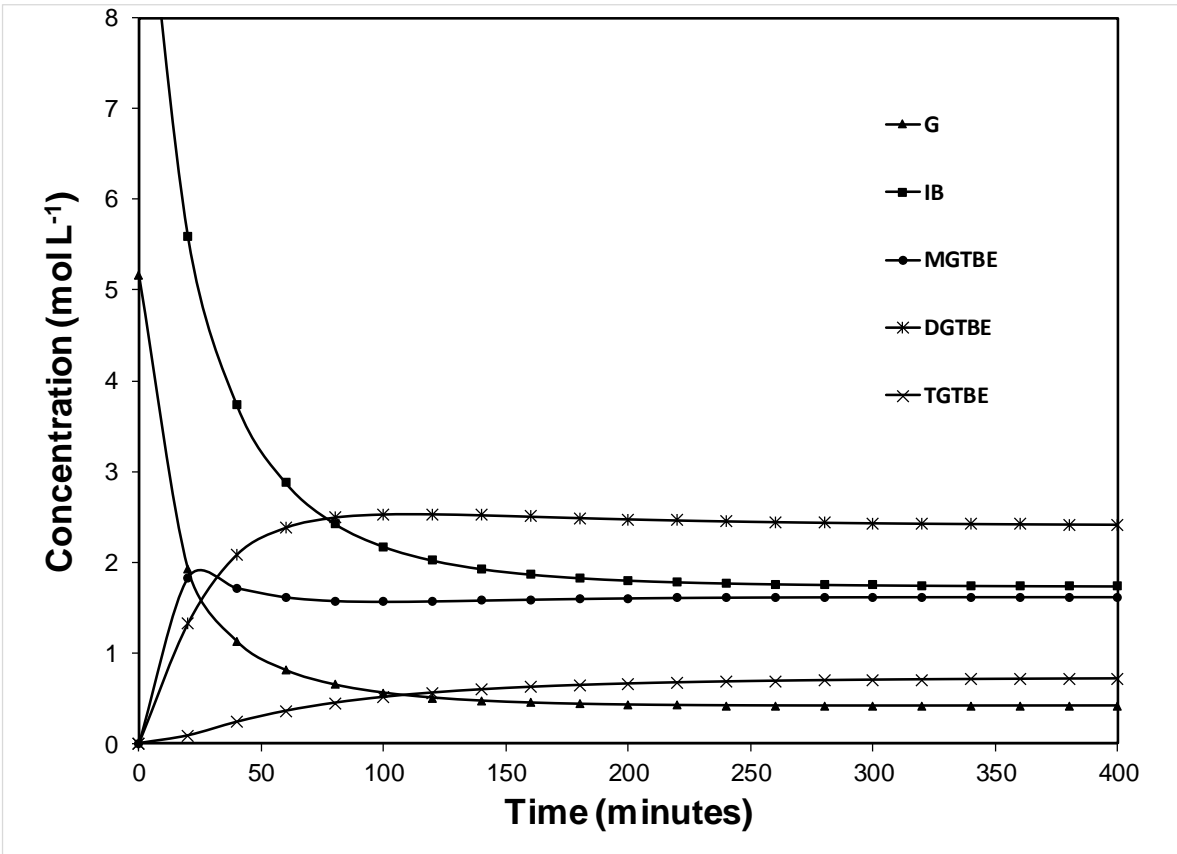


Figure 6S. Concentration profile at 353 K.

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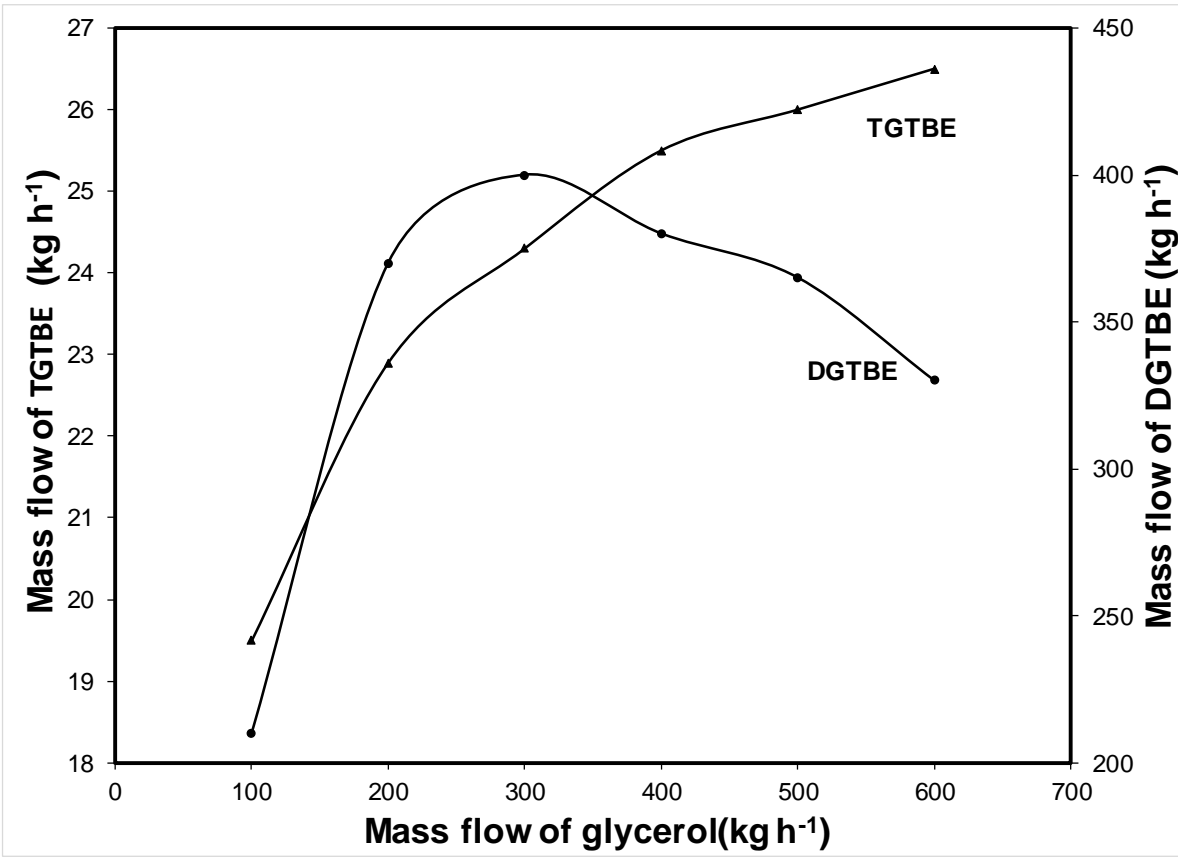


Figure 7S. Sensitivity test for the extractor unit.

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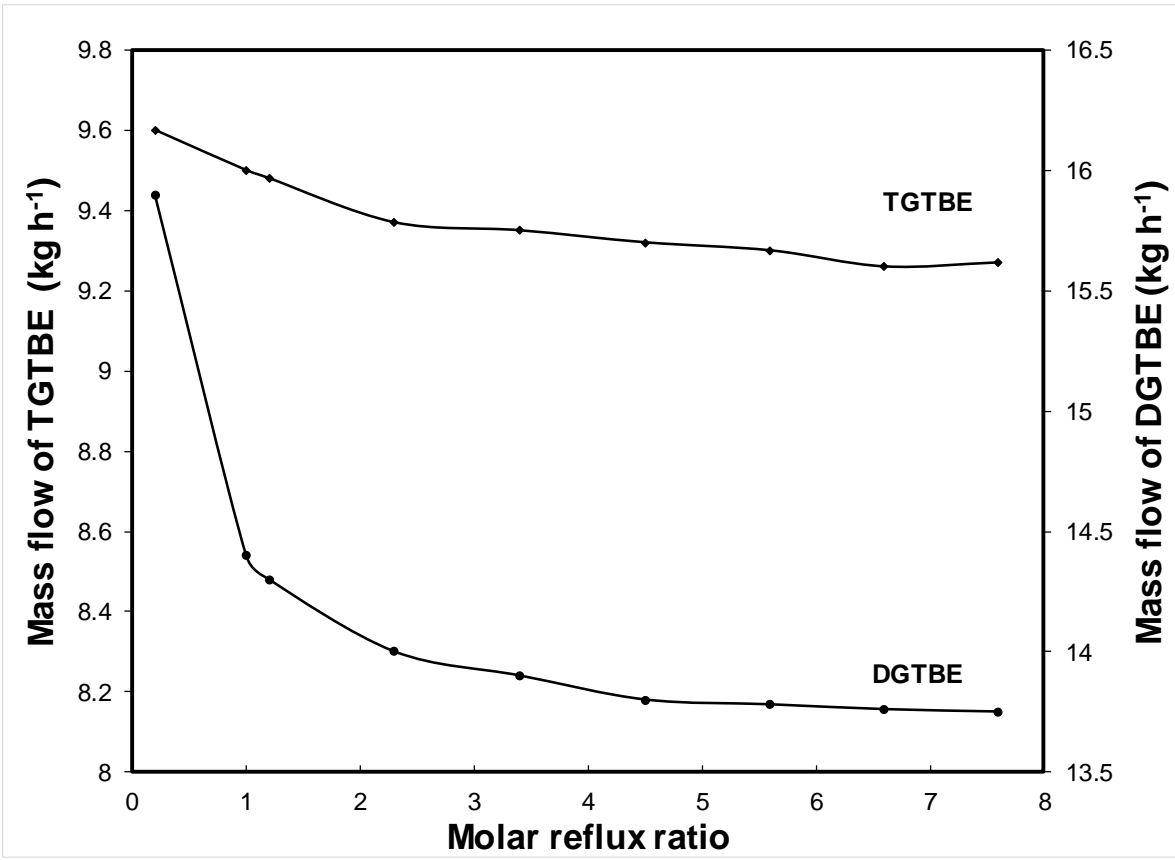


Figure 8S. Sensitivity test for the distillation unit.

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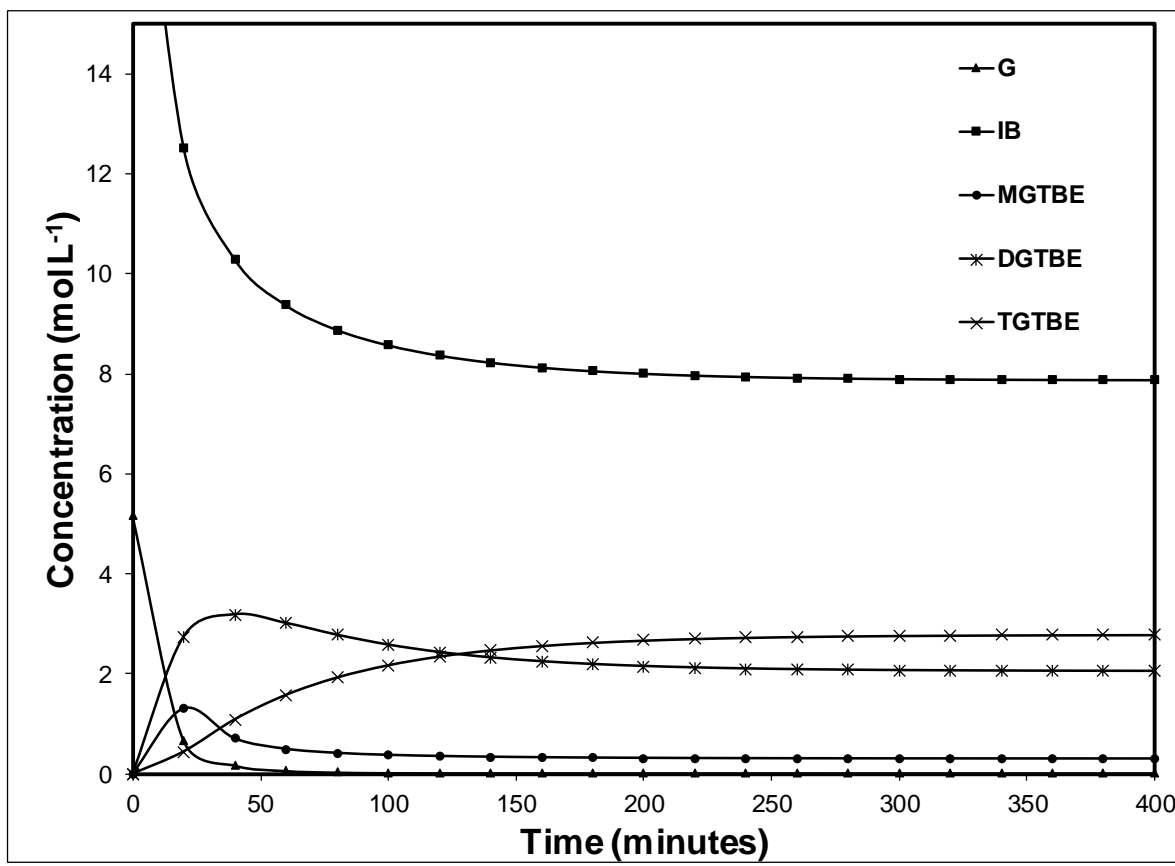


Figure 9S. Concentration profile for a 4:1 isobutylene: glycerol molar ratio.

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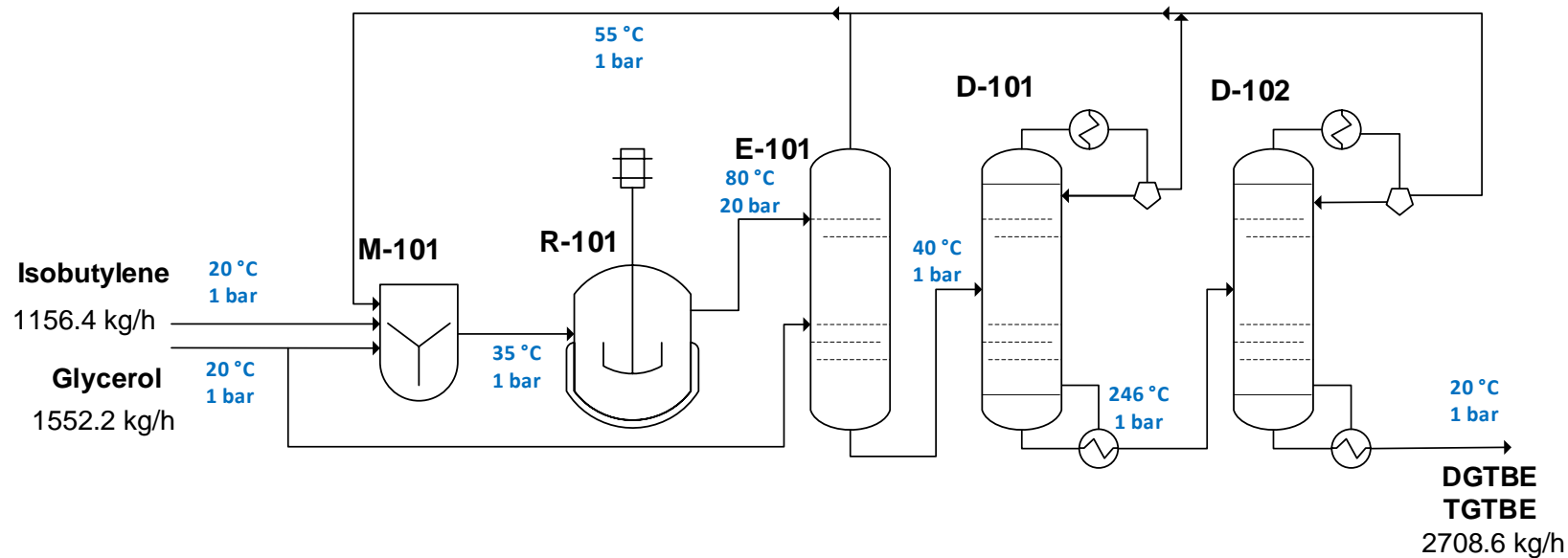


Figure 1.

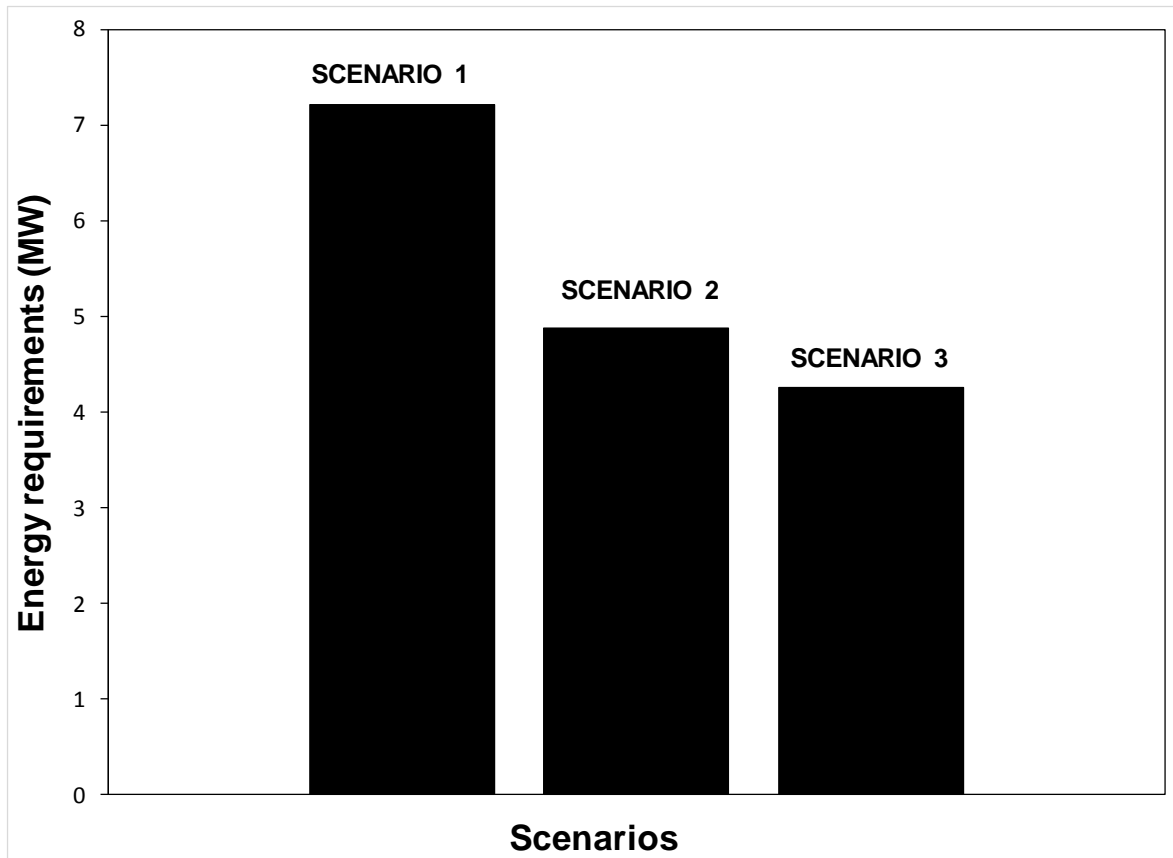


Figure 2.

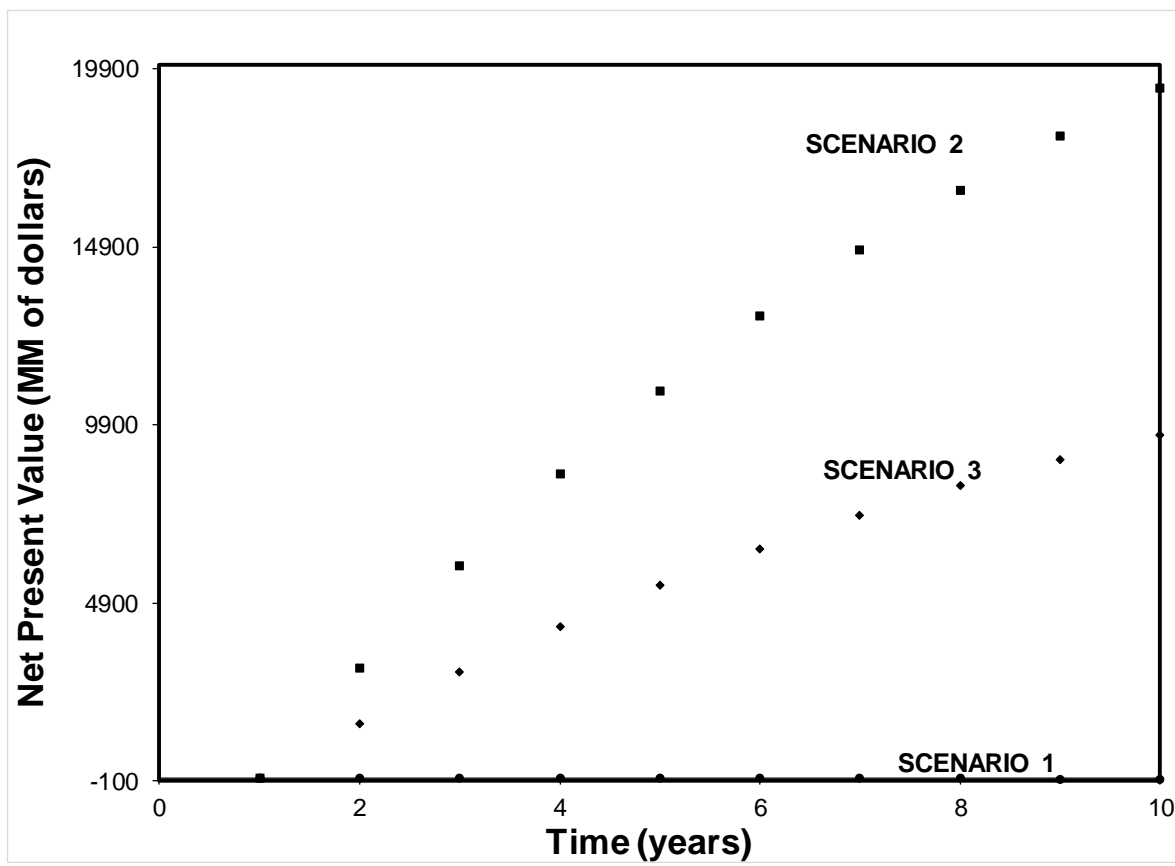


Figure 3

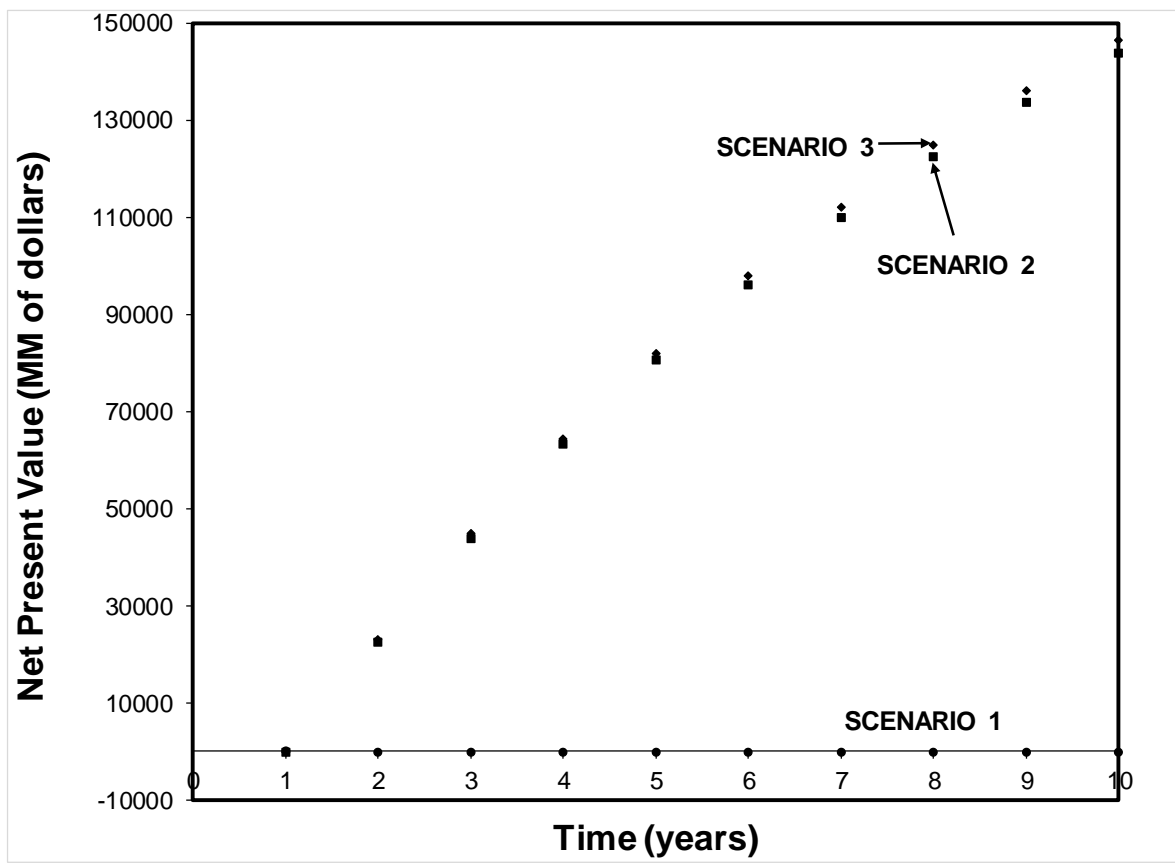


Figure 4.

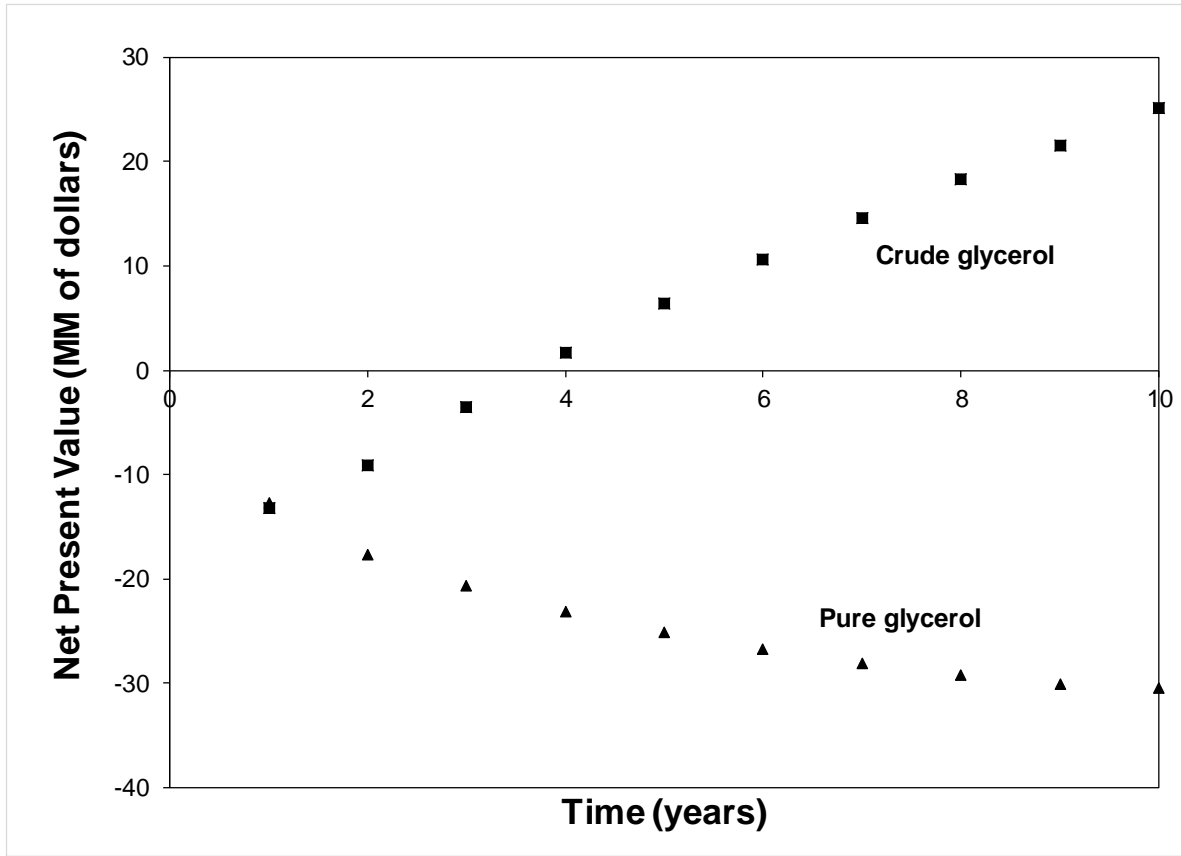


Figure 5