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FACULTEIT INDUSTRIËLE INGENIEURSWETENSCHAPPEN
master in de industriële wetenschappen: chemie

Masterproef

Study on the etherification of glycerol to produce glycerol tert-butyl ethers

Promotor :
dr. Rita DE WAELE

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Anke Zimmermann
Scriptie ingediend tot het behalen van de graad van master in de industriële wetenschappen: chemie

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Preface

This thesis was established in cooperation with Hanoi University of Science and Technology. It is therefore a great pleasure to thank Prof. Dr. Hong Lien and Dr. Vu for their support and engagement to help me finalize my thesis and offering me the possibility to do my project work at this incredibly kind and warmhearted university.

I am deeply thankful to Prof. Dr. Rita De Waele, who has always supported me, in both a moral and professional way. I really would like to thank her for always being the critical reader I needed, her valuable discussions really helped to improve this work.

I also would like to offer my sincere gratitude to the members of the GTBE-project: Quyen, Quang, Khoa and Tien. They were always the helping hand when I needed one and really made my life in Hanoi unforgettable.

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And last, but not least, my sincere thanks to my family and to all my friends in Vietnam and Belgium, who have always supported me and provided me with social and moral education.

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Nomenclature

d-GTBE	di-glycerol tert. butyl ether
DIPE	diiso-propyl ether
ETBE	ethyl tert. butyl ether
GC-MS	gas chromatography-mass spectrometry
GTBE	glycerol tert. butyl ether
IPTBE	iso-propyl tertiary butyl ether
m-GTBE	mono-glycerol tert. butyl ether
MTBE	methyl tert. butyl ether
TAEE	tertiary amyl ethyl ether
TAME	tertiary amyl methyl ether
t-GTBE	tri-glycerol tert. butyl ether

English abstract

Biodiesel production is rapidly increasing but will only be viable if the inevitable byproduct, glycerol, can be revalorized too. An interesting option is the conversion with tert. butyl alcohol (TBA) into a fuel additive: glycerol tert. butyl ether (GTBE). This oxygen rich ether can improve the combustion, which results in less CO- and soot-exhaust. This thesis investigates the possibilities of mono-GTBE (m-GTBE) as gasoline additive.

First, the etherification of glycerol with TBA is optimized to become a maximal yield of m-GTBE. The temperature (80-110°C), reaction time (2-6h) and catalyst loading relative to glycerol (5-10 wt%) are the observed parameters. After isolation by means of distillation, the m-GTBE is blended with commercial gasoline in percentages of 2.5, 5 and 7.5 v%. Finally, the influence on density, vapor pressure, boiling range and oxygen content is checked according to ASTM standard test methods.

The temperature affects the yield of m-GTBE positively while the time and catalyst loading show a negative effect. The density has increased. The vapor pressure has increased for 5% m-GTBE but decreased again for 7.5%.
In addition, boiling range and oxygen content augment.
These results indicate that m-GTBE could be a potential additive that positively affects the combustion characteristics of gasoline.

Dutch abstract

Door de stijging in biodieselproductie is er een overschot aan glycerol ontstaan. De etherificatie van glycerol met tert. butyl alcohol (TBA) biedt de mogelijkheid om glycerol nuttig aan te wenden en te transformeren in een brandstofadditief: glycerol tert. butyl ether (GTBE). Deze ether is zuurstofrijk en verbetert de verbranding, waardoor deze vollediger verloopt en er minder CO en roet gevormd worden.
Deze thesis onderzoekt de mogelijkheden van mono-GTBE (m-GTBE) als benzineadditief.

Eerst wordt de etherificatie van glycerol met TBA in een batchreactor geoptimaliseerd tot een maximale opbrengst aan m-GTBE. De temperatuur (80-110 °C), reactietijd (2-6h) en katalysator verhouding ten opzichte van glycerol (5-10 m%) ten opzichte van glycerol zijn de reactieparameters. Na isolatie van m-GTBE met behulp van distillatie volgt de toevoeging aan commerciële benzine in percentages van 2,5, 5 en 7,5 %. De invloed op dichtheid, kookpuntrange, dampdruk en zuurstofgehalte wordt nagegaan met behulp van standaard testmethodes.

De optimalisatie toont aan dat temperatuur de opbrengst aan m-GTBE positief beïnvloedt terwijl tijd en katalysator verhouding een ongunstig effect hebben. Tests op benzine wijzen uit dat m-GTBE de dichtheid doet stijgen, net als het kooktraject en zuurstofgehalte. De dampdruk stijgt voor 5% m-GTBE maar daalt onder de initiële dampdruk voor 7,5%.
Deze resultaten tonen aan dat m-GTBE een bruikbaar additief is dat een gunstig effect heeft op de verbrandingskarakteristieken van benzine.

1 Introduction

Since The U.S. Clean Air Act Amendments of 1990, a lot of research on fuel additives is conducted. The main goal of these additives is to improve the fuel combustion in engines and to minimize the air pollution. These organic compounds act as an octane booster and reduce the exhaust of particulate matter and carbon monoxide [1].

Renewable energy is another aspect of the environmental effort in the automotive industry to improve air quality, with biodiesel being one of the most frequently used biofuels [2]. The inevitable byproduct in the production process of biodiesel is glycerol.
Biodiesel is a promising, alternative fuel but will only be viable if the crude glycerol can be processed too. A very considerable way to revalorize glycerol is the production of alkyl-ethers of glycerol, which can be employed as oxygenated additives for fuel [1].
The closed cycle that is created when glycerol is converted into GTBE is visualized in Figure 1.

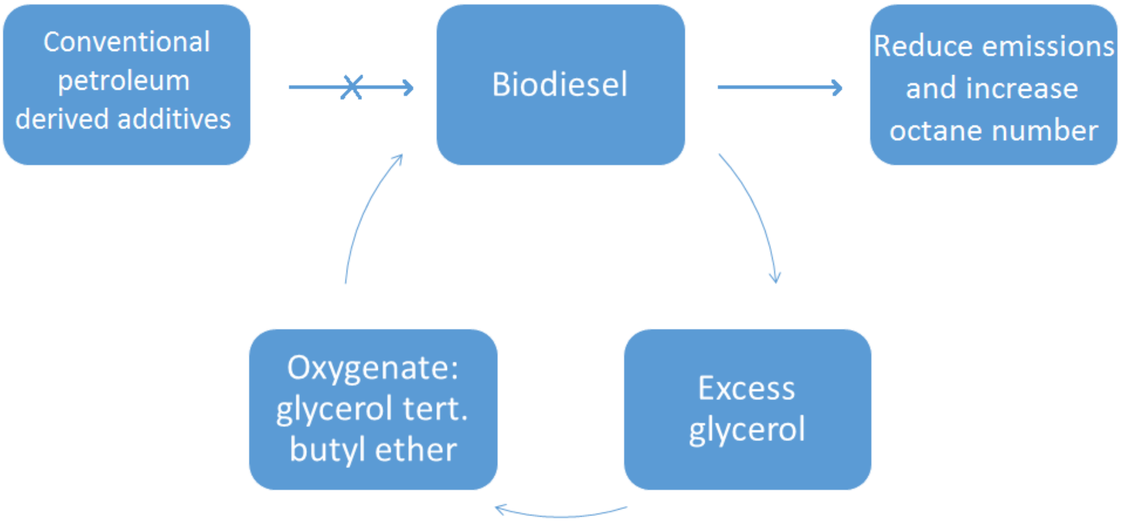


Figure 1: Visualization of the closed cycle for production of GTBE from glycerol

In this way, the material cycle can be closed and the glycerol tert. butyl ether (GTBE) can be added to petrol as well as to biodiesel again, to supersede the conventional petroleum derived fuel additives for reducing vehicular emissions and increasing octane number [3] [4].

Glycerol can be converted to GTBE through catalytic reaction with isobutene, ethanol or tert. butyl alcohol. GTBE is a mixture of mono-, di- and tri-tert-butyl ethers (m-, d-, t- GTBE). The etherification takes place at the presence of a homogeneous or heterogeneous acid catalyst, such as Amberlyst or Zeolite [5] .
Especially, the etherification reaction with tert. butyl alcohol is interesting because it can be carried out in the liquid phase without a solvent.

Due to the high oxygen content, combined with high octane numbers and good solubility, d-GTBE and t-GTBE are known as potential oxygenates for diesel fuel, substituting current oxygenates such as methyl tert. butyl ether (MTBE) and ethyl tert. butyl ether (ETBE), which are believed to be harmful for the environment and health [6]. In addition, due to the presence of oxygen in their structure, they might reduce the carbon monoxide and particulate matter emission from incomplete combustion.

m-GTBE could offer the same advantages but it cannot be used as oxygenate for diesel fuel due to its low solubility at room temperature.

In gasoline on the other hand, the solubility is sufficient, making m-GTBE a useful oxygenate for gasoline. However, the influence of m-GTBE on gasoline characteristics is not determined yet and a method for blending m-GTBE with gasoline still has to be developed [7]. These goals provide the foundation of my master thesis.

The first goal of the experiments is to determine the optimal conditions (temperature, catalyst loading with respect to glycerol and reaction time) for a maximal yield of m-GTBE in the reaction of glycerol with tert. butyl alcohol, using Amberlyst 36 Wet and Beta Zeolite as a catalyst.

Secondly, a way to isolate pure m-GTBE from the mixture has to be developed.

Thirdly, a recipe for blending the pure m-GTBE homogeneously with commercial gasoline needs to be elaborated and optimized so that the blend has a long term stability and no demixing occurs. Also, the amount of m-GTBE has to cause a significant effect on the characteristics of the gasoline.

Finally, the influence of m-GTBE on gasoline has to be determined by examining the amount and types of hydrocarbons and the octane number.

This thesis is divided into 4 parts. The first part focusses on earlier work and offers a complete literature review with the key aspects of GTBE. The second part covers the materials and methods section and gives a detailed description of the used materials and the followed procedures. In the third part, results will be discussed and finally, the conclusions and recommendations are given.

2 Literature review

2.1 Biodiesel

The demand for biofuels is currently on the rise worldwide with biodiesel being one of the most promising alternatives. It can effectively be used both when blended with fossil diesel fuel and in pure form [8]. The engine performance is generally comparable to that of conventional diesel fuel while the engine emissions of particulates, hydrocarbons and carbon monoxide are reduced [9].

Biodiesel consists of the simple alkyl esters of fatty acids, most typically the methyl esters and is produced from bio-resources, through transesterification of triglycerides with methanol or ethanol.
Homogeneous acid and base solutions are commonly used as a catalyst (NaOH, KOH, H_2SO_4).
The possibilities for bio-resources have increased: rapeseed can be used, sunflower seed oil, soybean oil but also used frying oils and animal fats [10].
The basic outline for the production of biodiesel is shown in Figure 2.

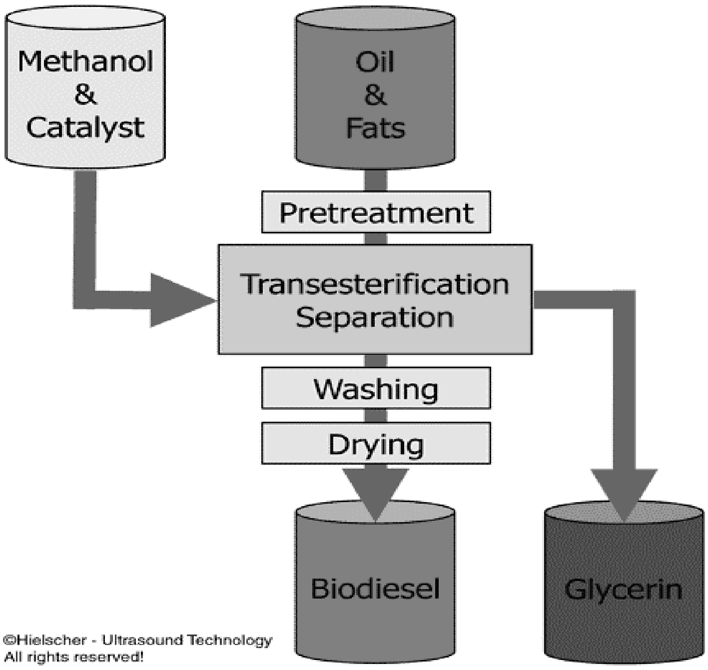


Figure 2: Basic outline for the production of biodiesel [11]

In a stoichiometric reaction, glycerol is created as a by-product and represents 10% v/v of the ester, one mole of glycerol is synthesized for every three mole of methyl ester. With an increasing biodiesel market, the glycerol reserves are increasing too. Biodiesel thus, will only be viable if value added products can be produced from glycerol.

2.2 Glycerol

Glycerol is a simple polyol which has a IUPAC-name of 1,2,3-propanetriol. It is also known as glycerin or 1,2,3-trihydroxypropane. The molecular structure is shown in Figure 3.

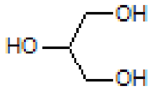


Figure 3: Molecular structure glycerol

Glycerol was chemically first discovered in 1779 by the Swedish chemist C. W. Scheele during the saponification of olive oil with lead oxide. However, it was M. E. Chevreul that introduced the name glycerol, referring to the Greek “glycos”, meaning sweet.

In Table 1, the properties of glycerol are displayed [12].

Table 1: Chemical properties of glycerol

Properties	**Values**
Chemical structure	CH_2OH-CHOH-CH_2OH
Molecular weight	$92.09 \frac{g}{mol}$
Color	Colorless
Melting point	17.9 °C
Boiling point (1 atm)	290 °C
Boiling point (50 mm Hg)	210 °C
Specific gravity	1.26050/4
Solubility in 100 parts Water Alcohol Ether	 Infinitely Infinitely Insoluble
Viscosity at 20 °C Pure glycerol 50 % glycerol in water	 1410 cP 6.00 cP
Surface tension at 20 °C	63.4 dynes/cm
Flashpoint of 99 % glycerol	177 °C
Fire point	204 °C
Auto-ignition point On platinum On glass	 523 °C 429 °C
Other characteristics	Sweet, hygroscopic

Natural glycerol is obtained by high-pressure hydrolysis or by transesterification.
In contrast, synthetic glycerol is produced from propene or from acrolein.
A third method is the oxidation from allyl alcohol by the Upjohn process.
Presently however, as mentioned before, the fastest growing source of glycerol is the production of biodiesel [3] [13].

To utilize the excess of glycerol created by the biodiesel industry, innovative methods are being developed, which can use glycerol as a building block for the production of value added chemicals. Figure 4 displays a schematic representation of a couple of possibilities [14].
It has to be noted that crude glycerol from the production of biodiesel has to be refined before it can be used in other processes.

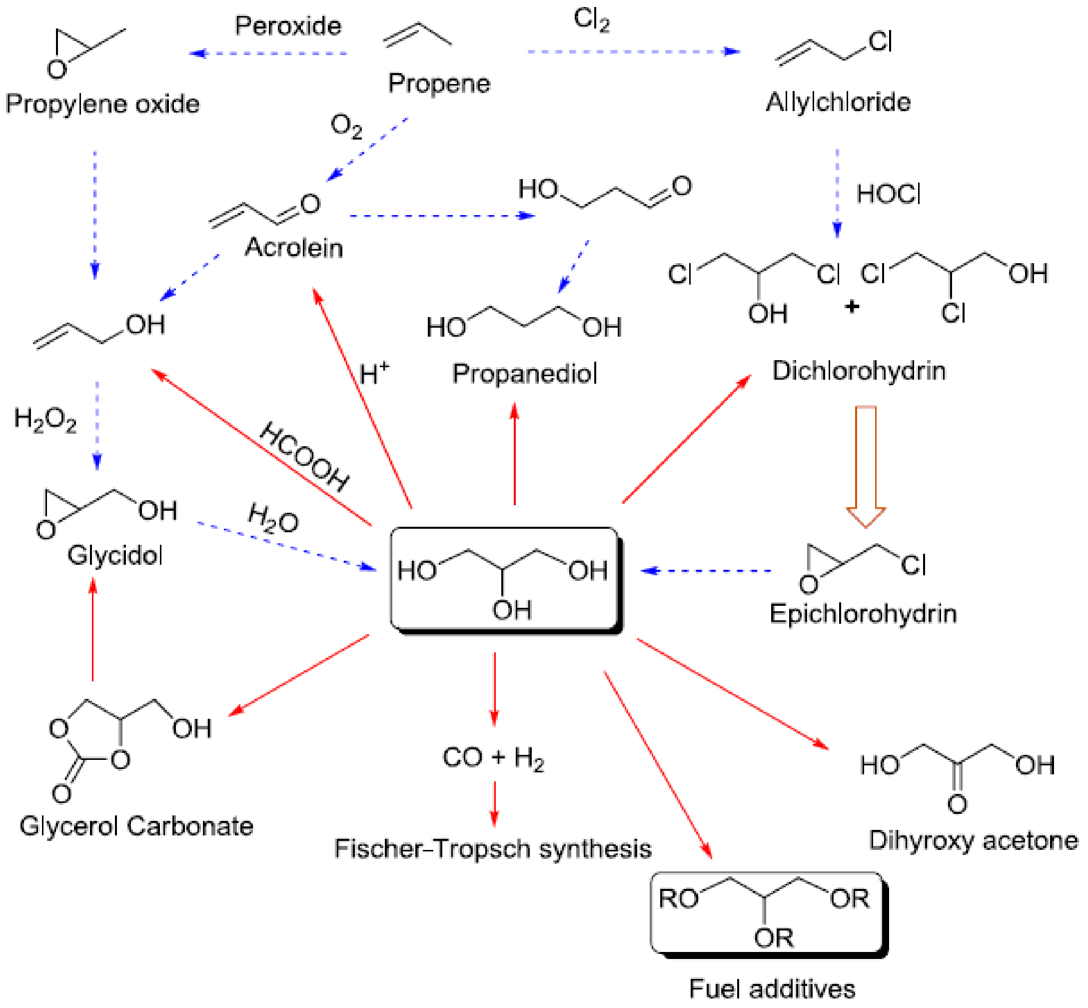


Figure 4: Possibilities for the use of glycerol [15]

Presently, the main source for the production of the above mentioned chemicals is propylene, which is a fossil fuel. Replacing the propylene by glycerol offers a possibility to diminish our fossil fuel dependency. However, this is only possible if the cost price of glycerol is much lower than the petroleum counterpart [15].

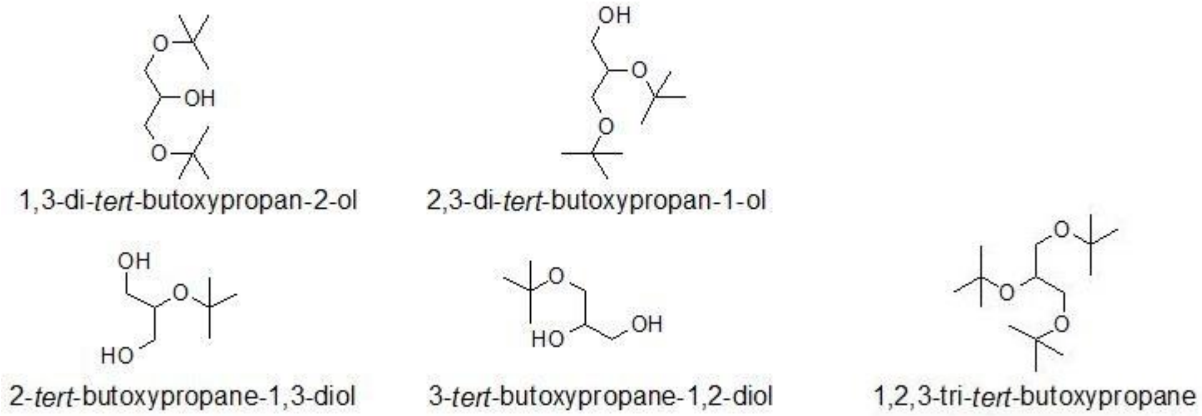
Since glycerol is an oxygen rich compound, the most effective way to use it would be as oxygenated additive for fuel. Glycerol itself however, cannot be added directly to fuel. Glycerol is hydrophilic and proceeds with polymerization at high temperatures, causing engine clogging and a reduction in engine speed. Moreover, glycerol can be oxidized to acrolein, which is noxious [16] or it can decompose. For all the above reasons, glycerol causes engine problems at high temperature [4]. Therefore, processes for converting glycerol to oxygenates, are developed.

The general process of converting glycerol to additives involves the deprotonation of a hydroxyl group of glycerol in the presence of heat and/or catalyst. In theory an acid based catalyst causes the protonation of the glycerol hydroxyl group, creating a leaving group. This is followed by a nucleophilic attack by the hydroxyl group of another glycerol molecule or substrate [11].

2.3 Production of glycerol tert. butyl ether

2.3.1 GTBE

Among several oxygenated additives proposed to blend with fuel, the ethers of glycerol could hold a prominent role [17]. In particular, tert. butyl ethers of glycerol (GTBE). GTBE is a mixture of 5 different structures, 2 mono-ethers, 2 di-ethers and 1 tri-ether. The chemical structure of the ethers and names is shown in Figure 5, together with their properties in Table 2.



1,3-di-*tert*-butoxypropan-2-ol

2,3-di-*tert*-butoxypropan-1-ol

2-*tert*-butoxypropane-1,3-diol

3-*tert*-butoxypropane-1,2-diol

1,2,3-tri-*tert*-butoxypropane

Figure 5: Product spectrum GTBE

Table 2: Properties m-, d- and t-GTBE [18]

Property	**m-GTBE**	**d-GTBE**	**t-GTBE**
Boiling point (K)	537.8	513.6	526.2
Critical temperature (K)	701.0	676.6	691.2
Critical pressure (bar)	28.16	19.66	13.06

From this table it is clear that m-GTBE has the highest boiling point, critical temperature and critical pressure.

Due to high oxygen content, together with high octane numbers, m-, d- and t-GTBE are potential octane boosters. Octane numbers of 112-128 (blending Research Octane Number) and 91-99 (blending Motor Octane Number) were reported [7]. When mono-ethers are the main product, even higher octane numbers were observed.
In addition, these oxygen-rich compounds can reduce carbon monoxide and particulate matter emission caused by incomplete combustion.

Tert. butyl ethers with a high content of di- and tri-ethers are considered promising as oxygenated additive for diesel fuels. Mono-tert. butyl ether is more polar, has a low solubility in diesel and therefore cannot be used in diesel fuels. It has a good miscibility with water which can also cause problems in the engine.
Consequently, during the etherification of glycerol, the formation of the so called higher ethers, di- and tri-ethers is addressed when the purpose is to synthesize GTBE as diesel additive. In contrast to these higher ethers, the possibilities of m-GTBE have barely been investigated up to now. m-GTBE has a higher octane number and is soluble in gasoline so theoretically, it could even be a better oxygenate.

In attachment 1, results of a molecular spectroscopic study carried out by Jamroz et Al. [19] are added. This attachment includes EI-mass spectra, FTIR spectra and FTRaman spectra, listing typical peaks for d- and t-GTBE. These characteristics can be used when analyzing samples of GTBE with GC-MS for example, since no official MS-spectra have been released yet.

2.3.2 Possibilities for the etherification of glycerol

Glycerol etherification reactions can be performed with different olefins and alcohols, mainly isobutene and tert. butyl alcohol. These reactions will be discussed in this chapter.

Reaction of glycerol with tert. butyl alcohol

One way to produce tert. butyl ethers is the catalytic reaction of glycerol with tert. butyl alcohol. This appears to be very attractive since it is a solid-liquid process, using TBA both as a reactant and solvent. The excess of TBA is used as solvent, thus the etherification is carried out in a homogeneous phase.

The reaction product is a mixture of m-, d- and t-GTBE. The general reaction and possible products for the reaction of glycerol with TBA are shown in Figure 6.

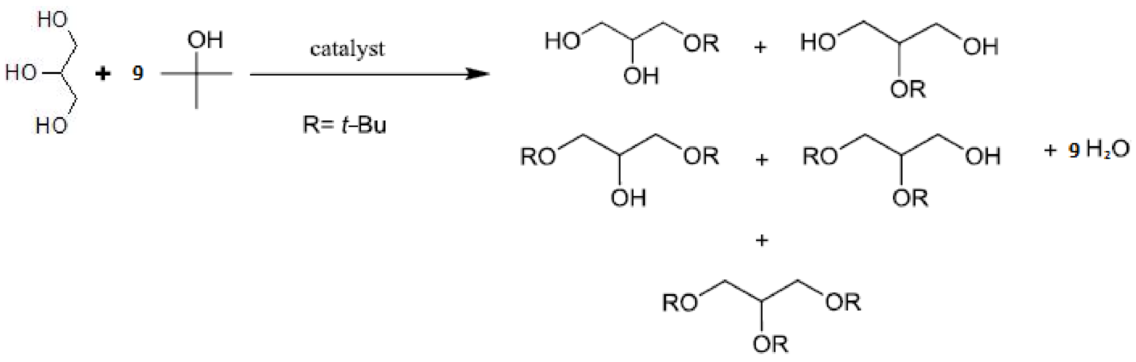


Figure 6: Possible products for reaction of glycerol with tert. butyl alcohol

In the presence of an excess of TBA, acid catalysts react with TBA to form a stable tertiary carbocation, while losing water. The formation of the carbocation is a reversible reaction. In absence of water or a suitable nucleophile, the carbocation can lose a proton to form isobutene. This reaction is reversible. Figure 7 shows the progress of the reaction.

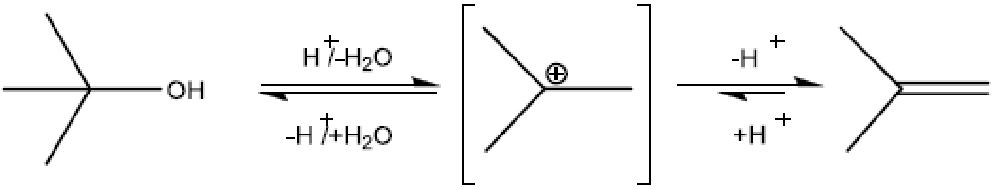


Figure 7: Formation of tert. butyl carbocation

In the presence of glycerol however, tert. butyl carbocation can act as electrophile. The carbocation can react with the alcohol functions, leading to 2 new intermediaries, as depicted in Figure 8.

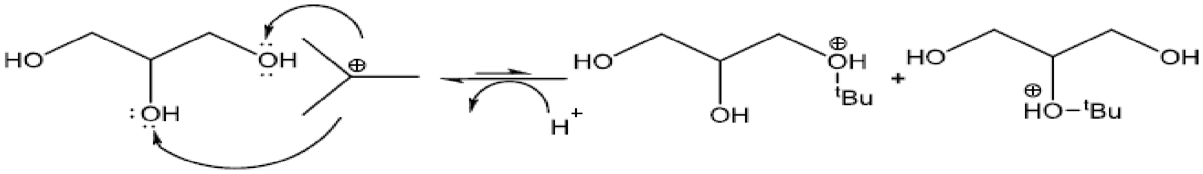


Figure 8: Nucleophilic attack of glycerol on carbocation

The left intermediary is preferred because the primary hydroxyl group is sterically less hindered (tert. butyl groups are voluminous) and is statistically favored (there are two primary hydroxyl groups and only one secondary). Therefore, it is more likely to form 1- and 1,3-ethers than 2- and 1,2-ethers.

The intermediary then can react to form m-, d- and t-GTBE as shown in Figure 10 and Figure 11.

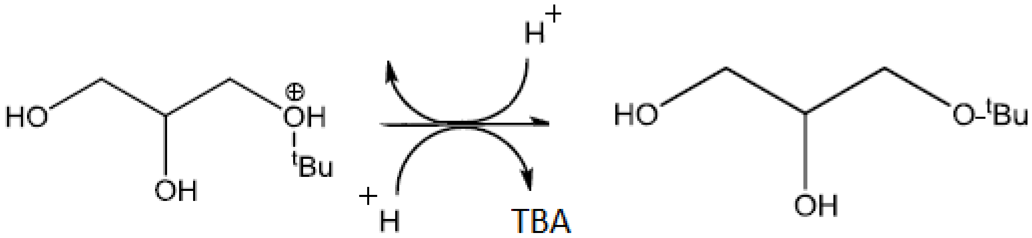


Figure 9: Formation of m-GTBE from intermediary

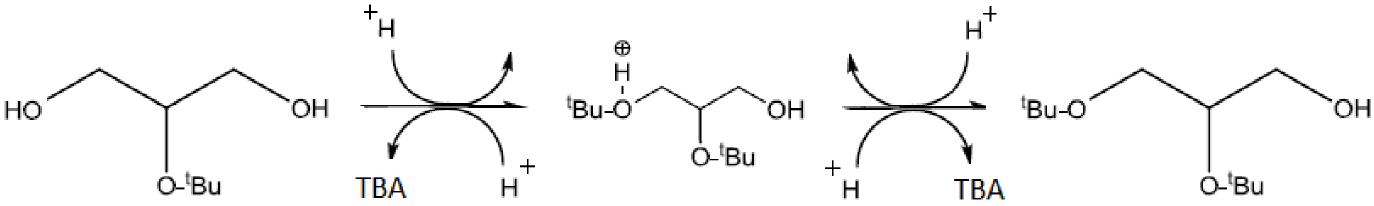


Figure 10: Formation of d-GTBE out of 1-ether

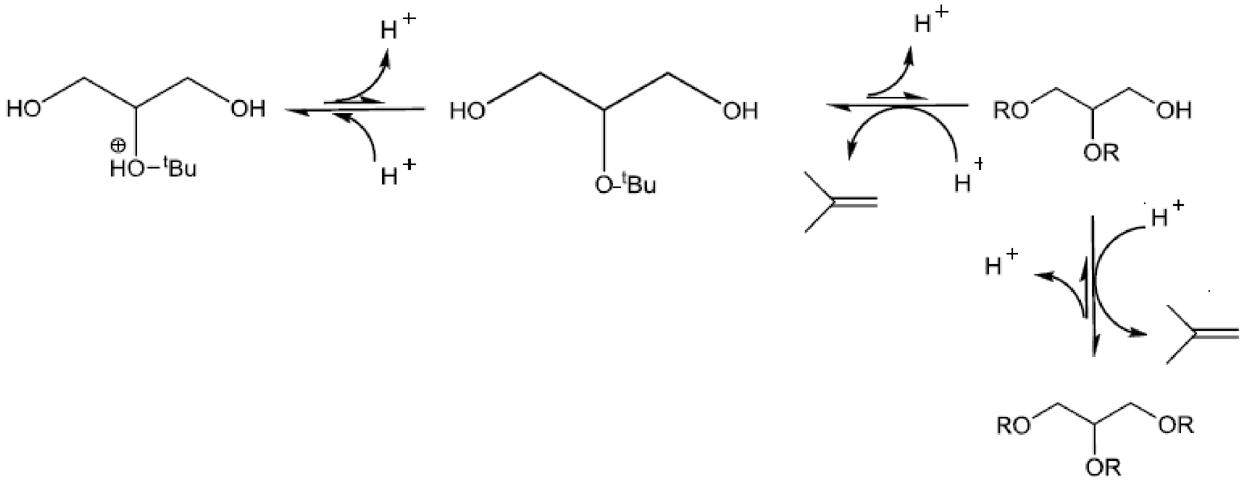


Figure 11: Formation of d- and t-GTBE out of 2-ether

The rate determining step is the formation of the tert. butyl cation. Therefore, the rate of reaction increases with the increase in acidic concentration. This explains the fact that a large excess of tert. butyl alcohol is necessary to compensate escaping isobutene [15].

Remarks about reaction of glycerol with TBA and side reactions

The formation of t-GTBE is limited due to steric hindrance.
By dehydration of TBA, isobutene can be formed as shown earlier in Figure 7. This isobutene can react with glycerol to form GTBE, as described later in this thesis [20].
The water released during TBA dehydration can hydrolyse the ethers resulting again in the formation of glycerol [5].

When using TBA as reactant, more water is produced than when using isobutene as reactant, which influences the thermodynamic equilibrium and limits the maximal conversion [2]. The water content increases as the TBA and glycerol contents decrease. With the decrease of TBA and increase of temperature, an increase of isobutene (formed out of TBA) can be observed.

Another possible side reaction is the dimerisation of isobutene (formed from dehydration of TBA), resulting in the products displayed in Figure 12.

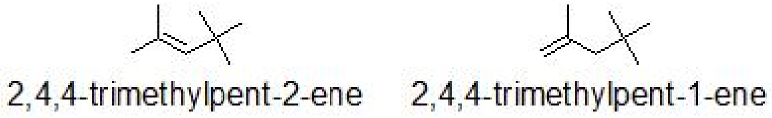


Figure 12: Dimerisation products from isobutene

Frusteri et Al. [21] focused on the etherification of glycerol with TBA over different solid acid systems and observed that the glycerol conversion linearly increases with reaction temperature. This can be explained by the increased kinetic constants. The increase for di-ether is more significant than for mono-ether because the mono-ethers are formed in a serial step and serve both as a product and a reactant. It is import to remark that these results are only valid within specific temperature ranges. When the reaction temperature reaches higher values (363 K), the de-etherification reaction becomes more important and the conversion stagnates.

The experimental rate law determined by Frusteri et Al. [21] was:

$$reaction\,rate = k \cdot [Gly]^{0.3} \cdot [TBA]^{1.7}$$

This rate law confirms the importance of TBA concentration and the suggestion that the formation of a tertiary carbocation from tert. butyl alcohol is the rate determining step. This carbocation will react with the glycerol, which is strongly adsorbed on the catalyst, as shown before in Figure 8.

For the tert. butylation of glycerol, the best catalysts are very acid ion-exchange resins with a high degree of crosslinking with large diameter pores. [5]
The highest yield of di- and tri-ethers is obtained over Amberlyst 36 at 60 °C [22].

Reaction of glycerol with isobutene

The synthesis of tert. butyl ethers can also be carried out using isobutene (IB) and glycerol on ion-exchange resins. Similar to the reaction with TBA, a mixture of m-, d- and t-GTBE is formed. Isobutene is produced by catalytic cracking, steam cracking and by dehydrogenation of isobutane [21].
The drawbacks of using isobutene as reactant are the complex three-phase system and the necessity for a suitable solvent to dissolve glycerol.
Commonly used solvents include dioxane and dimethyl sulfoxide [21].

In Figure 13, a general survey of the reactants with possible products is given.

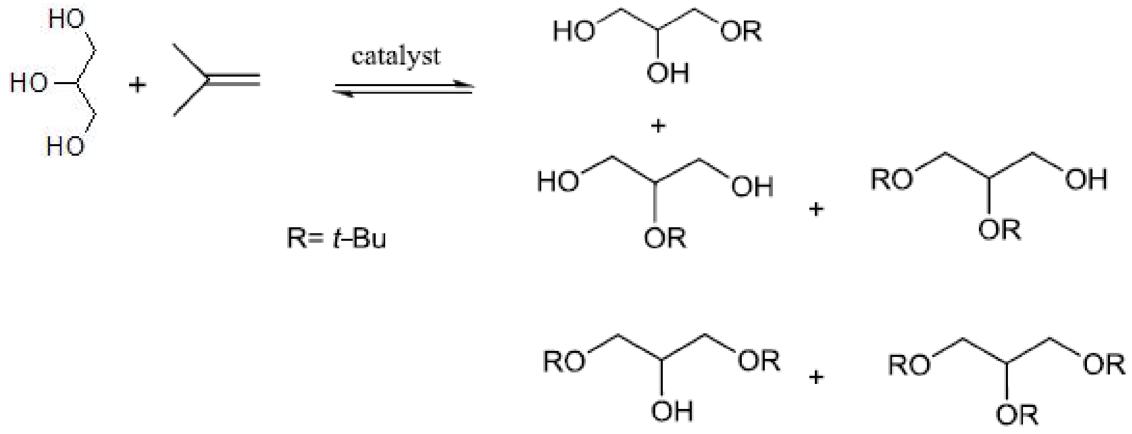


Figure 13: Possible products for reaction of glycerol with isobutene

The etherification of glycerol with isobutene follows the same consecutive reaction path as the reaction of glycerol with tert. butyl alcohol. The consecutive reactions are shown in Figure 14, Figure 15 and Figure 16.

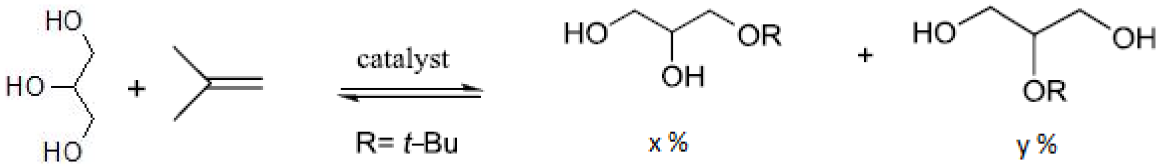


Figure 14: Reaction glycerol with IB to form m-GTBE

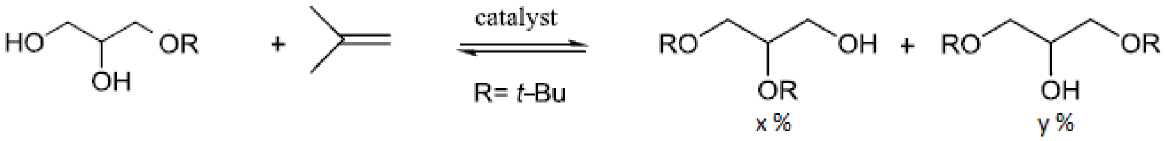


Figure 15: Reaction m-GTBE with IB to form d-GTBE

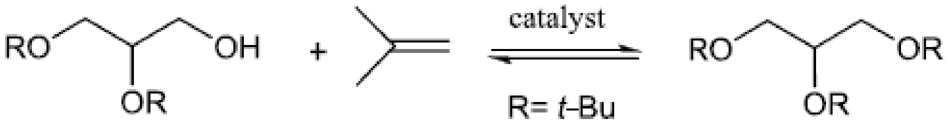


Figure 16: Reaction di-GTBE with IB to form t-GTBE

The reaction mechanism includes the same steps as the reaction with TBA, described earlier. Reaction of glycerol with isobutene is also preferred on primary hydroxyl groups due to sterical hindrance and statistics.
A higher reaction temperature leads to undesirable secondary reactions from isobutene, which are represented in Figure 17.

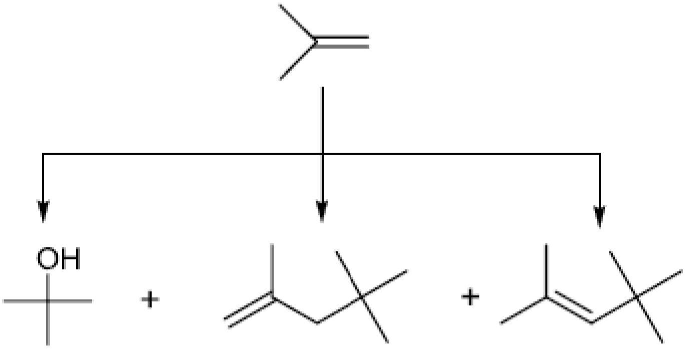
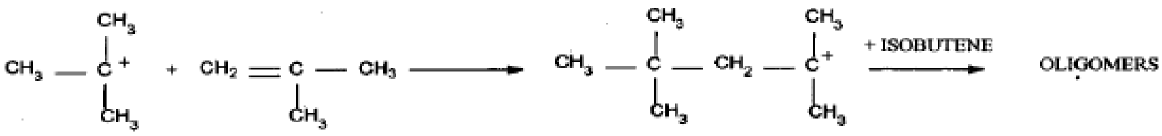


Figure 17: Possible side reactions starting from isobutene

Isobutene can convert to TBA and C8-alkenes.

Another side reaction that can occur in etherification is the oligomerisation of TBA and isobutene, which is shown in Figure 18.



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C^+}} + CH_2=\underset{\underset{CH_3}{|}}{C}-CH_3 \longrightarrow CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C^+}} \xrightarrow{+\text{ISOBUTENE}} \text{OLIGOMERS}$$

Figure 18: Oligomerisation of isobutene

Klepacova et Al. concluded from their research that the oligomerisation and hydration of isobutene are independent side reactions [5].

Research shows that the reaction pressure significantly affects the reaction kinetic, since the tert. butyl cation concentration in the liquid phase is determined by the equilibrium between the produced TBA (undesired by-product, as seen in Figure 17) and isobutene.

The reactions are slightly exothermic. The values of enthalpy, Gibbs free energy and equilibrium constants are displayed in Table 3 [18]. The entropy declines because gas transforms into liquid.

Table 3: Constants for etherification of glycerol with isobutene

Reaction	**ΔH (kJ/mol)**	**ΔG (kJ/mol)**	**K_{eq} (90°C)**
Gly + IB → m-GTBE	-47.25	9.88	0.038
m-GTBE + IB → d-GTBE	-40.86	0.052	0.98
d-GTBE + IB → t-GTBE	-27.30	15.60	0.0057

2.3.3 Catalysts

A fast reaction rate can be achieved by using homogeneous acids, such as H_2SO_4 or p-toluene sulfonic acid. However, the shortcomings are the severe pollution, corrosion and high separation costs.
The use of heterogeneous acid catalysts can eliminate these disadvantages: they can easily be separated from products and can repeatedly be used without neutralization. Several solid acid catalysts have been reported [5] [21] [22].

A strong acid ion exchange resin, such as Amberlyst 15, has large interconnected pores and a high concentration of strong acid sites. It is effective and affords a good conversion and selectivity of glycerol to d- and t-GTBE. Disadvantages are the thermal fragility and the fact that deactivated resin catalysts cannot be regenerated.

Another possibility for heterogeneous catalysts is the use of large-pore zeolites. They possess a negatively charged framework and a higher thermal stability. H-beta-Zeolite contains a high external surface area and is more active than other zeolites for glycerol etherification. Moreover, reactions over H-Beta zeolite run faster with high selectivity to di-ethers. In spite of the large pores, the formation of t-GTBE is still sterically hindered.
Etherification mainly occurs on the Brönsted acidic sites. Zeolites acidic properties can be adjusted by surface modification, such as sulfated zirconia modification, citric acid treatment and ion-exchange with rare-earth cations. [6]

The incorporation of organosulfonic groups over mesostructured silicas has generated another group of effective solid acid catalysts, enhancing the catalytic properties in contrast with conventional homogeneous and heterogeneous acid catalysts. Currently, these high external surface materials represent the best systems for the etherification reaction. The accessibility of acid sites plays a vital role in promoting catalyst activity and the systems with large pores perform the reaction at a higher rate.

For the etherification of glycerol, the most used catalyst include Amberlyst and Zeolite.

Beta Zeolite

Zeolites structure in general is a three dimensional network of SiO_4 and AlO_4 tetrahedra, linked to each other by shared oxygen atoms. The structure includes interconnected voids, which are occupied by water molecules and by cations [1].

Beta Zeolite, a synthetic zeolite, is a crystalline aluminosilicate with large pores. It has two different types of channels: straight 12-membered ring pores (6.6 x 6.7 Å) and zig-zag 12-membered ring pores (5.6 x 5.6 Å). The structure from different perspective views is shown in Figure 19.

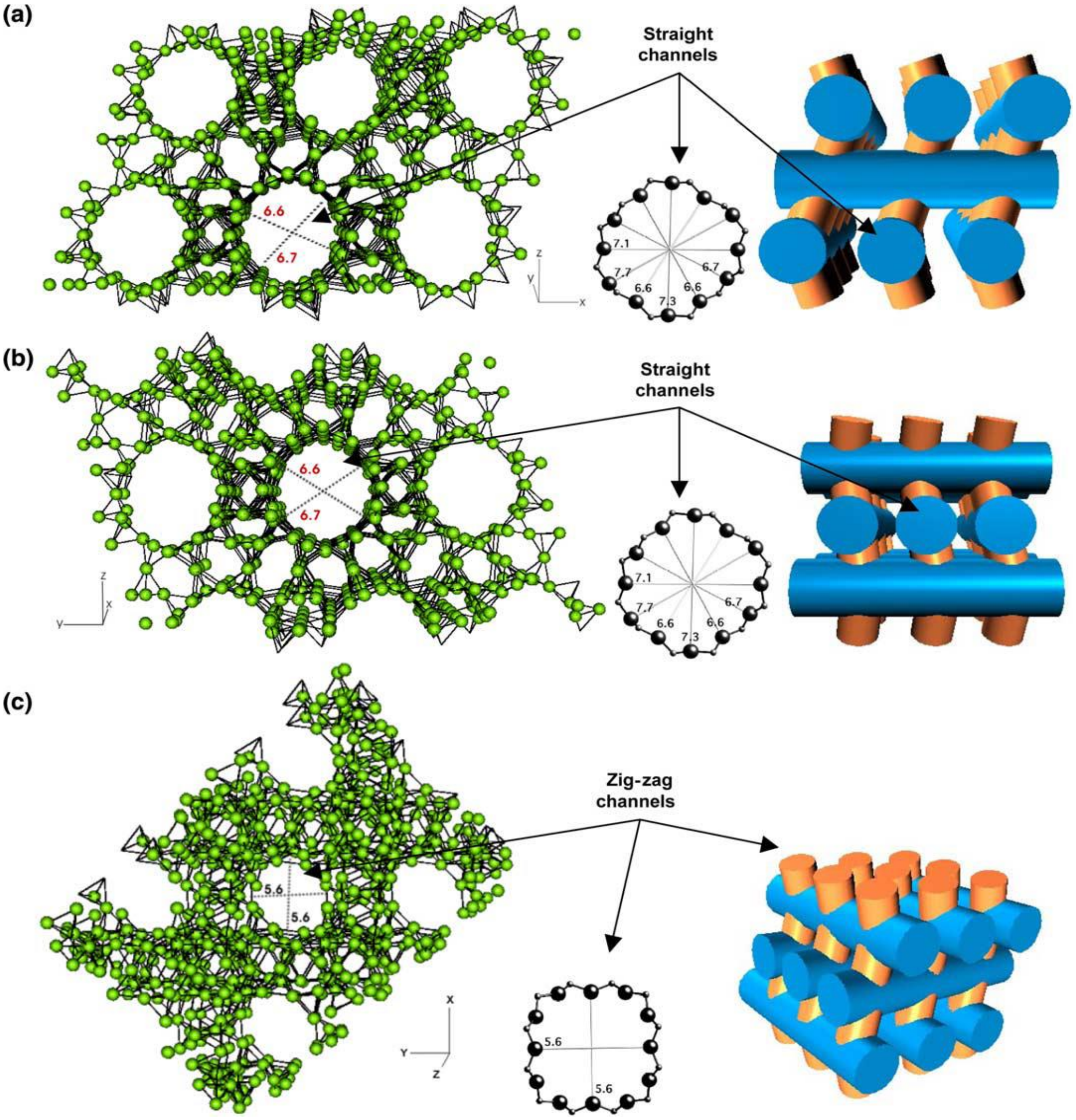


Figure 19: Stereographic drawings (left) and perspective views (right) of Beta Zeolite [1]

The left figures illustrate stereographic drawings. The spheres represent the oxygen atoms and the tetrahedron. They surround the tetrahedrally coordinated Si- or Al-atoms.

The perspective views show the pore network of Beta Zeolite. The cylinders represent the pores of Beta Zeolite and facilitate the visualization of the intersection between straight and zig-zag channels. The aluminum can create Brönsted as well as Lewis acidity. Brönsted acidity is present on the external surface and on the internal surface while Lewis acidity is mainly present on the internal surface.

The interesting part for the etherification of glycerol is the so-called reactant shape selectivity. If a molecule it too big, it cannot diffuse through the pores and reach the active sites to react. Considering the size of glycerol (0.515 nm), the pore entrances should at least be 0.515 to allow the glycerol molecules to enter and reach the active sites [1]. As described earlier, the pores are at least 0.55 nm. Other catalysts have a higher pore diameter (e.g. Amberlyst 36Wet® has a pore diameter of 24 nm). This relatively small pore diameter makes Beta Zeolite the perfect choice when the formation of m-GTBE is favored: d- and t-GTBE are larger molecules and are too big to enter and reach the active sites.

2.3.4 General remarks

Many research is carried out to determine optimal conditions for the etherification of glycerol using different reagents and catalysts.
Besides determining the optimal conditions, some general facts and trends can be remarked.

Previous studies have pointed out that increasing the TBA/Gly-ratio from 3/1 to 4/1, causes an increment in glycerol conversion. However, further increasing the loading from 4/1 to 5/1 has a lower effect on the conversion. The same conclusions can be drawn when using isobutene as reactant [2].

Excess of isobutene enhances the oligomerisation whereas an excess of glycerol causes the viscosity of the reaction mixture to increase. High viscosity affects the mass transfer between liquid solution and catalyst and therefore, limits the reaction rate.

The addition of TBA to the reaction mixture of glycerol and isobutene can hinder the oligomerisation reactions and eliminate the mass transfer limitations, improving the selectivity and yield.

A progressive decrease in m-GTBE is observed as a function of reaction time. This can be explained by the multiple-step-character of the etherification.
Without catalyst, no reaction takes place. Amberlyst was shown to be the most active catalyst for the formation of m-GTBE. The highest selectivity for m-GTBE is achieved at low conversion level as well as with low isobutene/glycerol loading [5] [23] [15].
The general yield arises when the amount of catalyst increases, with 7.5 wt.% giving the optimal yield for etherification.
Further increase of the catalyst weight leads to a limitation of conversion by the growing formation of water, which counterworks the etherification equilibrium. However, the formation of water hinders the extent of oligomerisation and makes it difficult to obtain higher ethers. Water also competes with TBA and glycerol on the active sites adsorption of the catalyst. The design of a water-removing reaction medium could increase the formation of the higher ethers.

To describe the kinetic mechanism, the Langmuir-Hinshelwood mechanism was found to get the best fit with experimental data. The general idea of the Langmuir-Hinshelwood is that all reactants are adsorbed on the catalyst surface before chemical reaction takes place [24].

2.3.5 Process design

For the production of GTBE, several processes were developed and different designs are possible. In the following section, some typical designs will be explained.

Traditional design and control of GTBE production using TBA

In the conventional production of GTBE, a typical reactor-separation-recycle model is used. [25]

Typically, reactants are brought into contact with solid catalysts at the appropriate process condition. This can be done in multiple steps. The next step is the separation: unconverted reactants are separated from the products, mostly by multiple distillation steps. In some cases, the unconverted reactants can be recycled to the reaction section. [25]

An example for the production of d- and t-GTBE is shown in Figure 20.

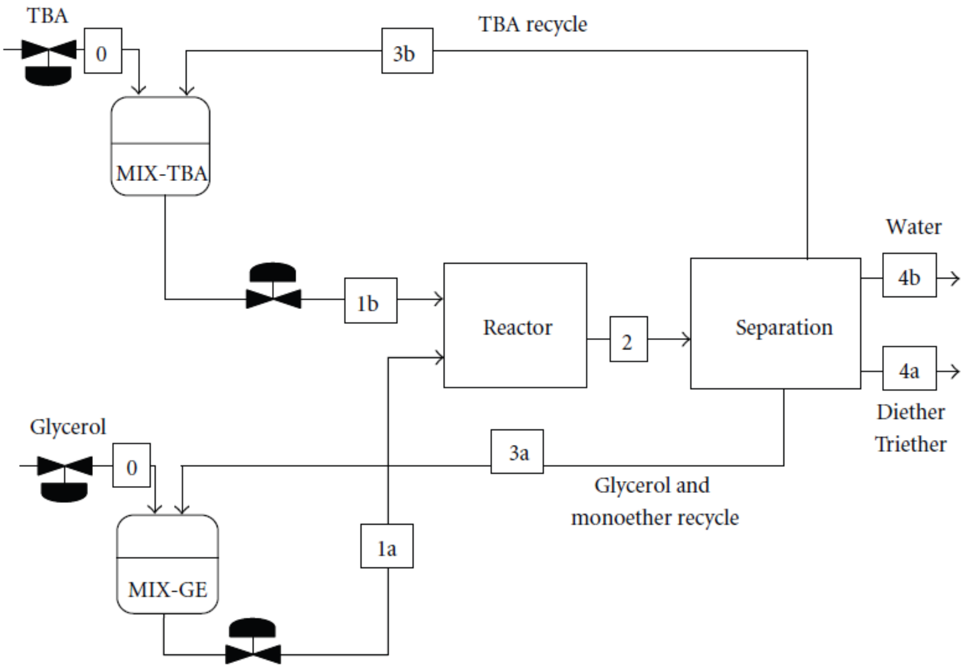


Figure 20: Reactor-separation-recycle process for glycerol etherification plant [25]

After reaction in a plug flow reactor, the effluent enters the separation section. Here, d-, t-GTBE and water are removed from the plant. Glycerol and m-GTBE are recycled to the reactor, after being mixed with fresh reactants.

Table 4 presents the boiling points of the main compounds in the process. t-GTBE is barely produced and therefore, not included [25].

Table 4: Boiling points products etherification of glycerol [25]

Component / Azeotrope	T (°C)	Destination
Isobutene	-6.25	By-product
TBA	82.42	Recycle
Water	100	By-product
d-GTBE	240.4	Product
m-GTBE	256.61	Recycle
Glycerol	287.85	Recycle

Small amounts of isobutene that are formed during the reaction can easily be removed due to their lower boiling point. TBA and water form an azeotrope and are removed from the glycerol-ether mixture by distillation. In a next distillation step, glycerol and m-GTBE are obtained as a bottom product and will be recycled.

To get d-GTBE with a high purity seems difficult, because of the low boiling Glycerol/d-GTBEazeotrope. Using a residue map can solve this problem. The residue map of d-GTBE/m-GTBE/Glycerol is shown in Figure 21 [25].

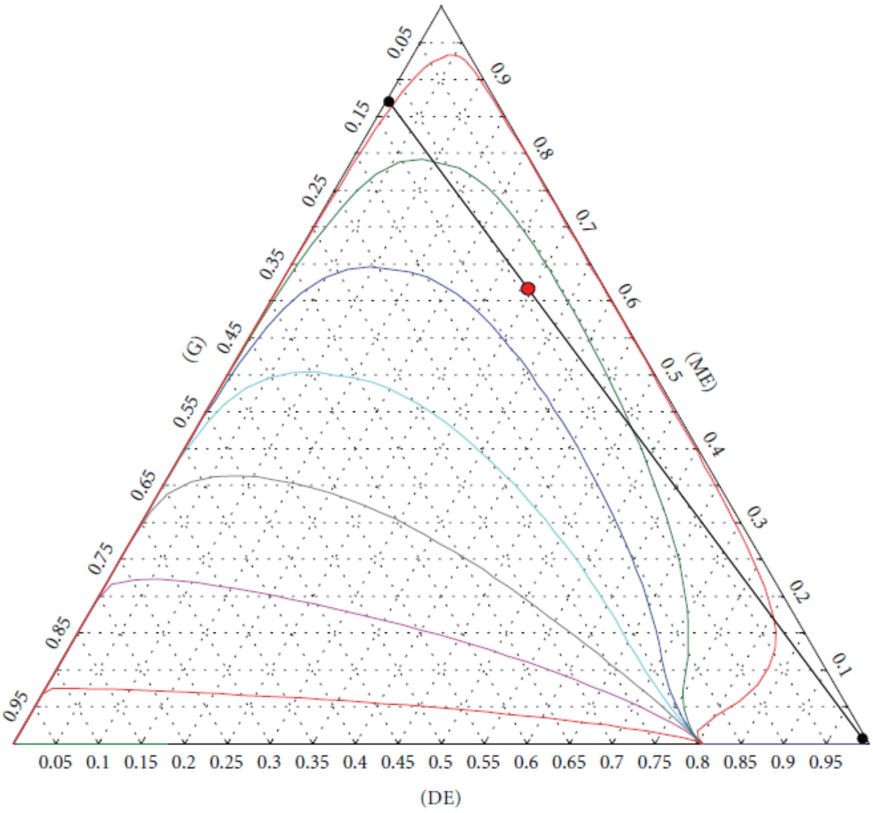


Figure 21: Residue Curve Map of glycerol-m-GTBE-d-GTBE [25]

Figure 18 shows there is one distillation region where m-GTBE acts as a solvent for glycerol. This allows d-GTBE to be obtained in high-purity.

To break the water/TBA azeotrope, a suitable solvent is added, for example 1, 4-butanediol. First, the stream is separated in TBA and azeotrope. Afterwards, the azeotrope is sent to an extractive distillation column, where the solvent is fed at the top and the azeotrope enters in the lower part. The distillate contains water, while the bottom stream consists of solvent and TBA, which are separated afterwards. The residue curve map of the mixture is shown in Figure 22.

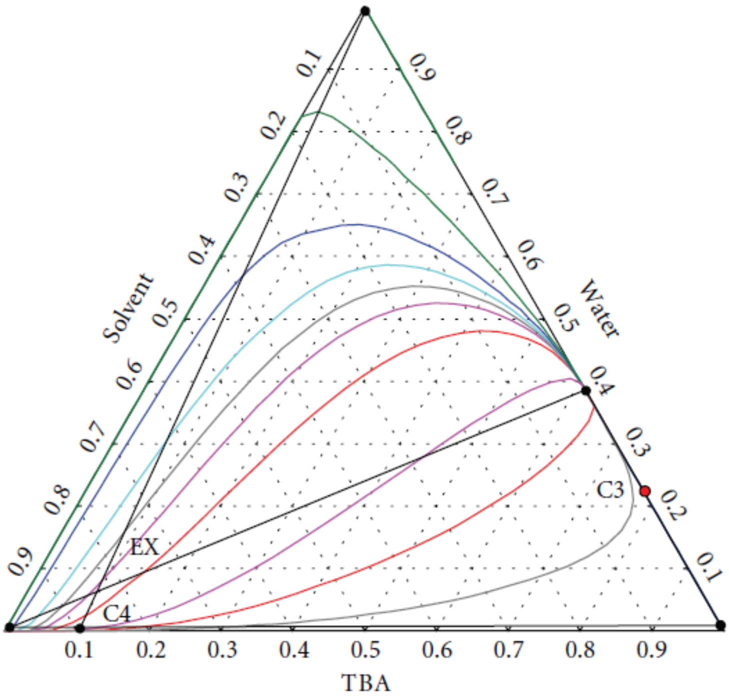


Figure 22: Residue Curve map of TBA-Water-1, 4-butanediol mixture: [25]

An economic evaluation of the process was performed, considering a 10 years payback time. The total annual energy cost would be 1178 000 $/year [25].

Reactive distillation (RD)

Reactive distillation is a process that combines the reaction and separation into one single step. The industrial applications of reactive distillation have been well recognized and perhaps considered as the most successful concept of multifunctional reactors. It is one of the favor processes for the synthesis of octane enhancers like methyl tert. butyl ether and tert. amyl methyl ether.
Recently, the application of RD for the etherification of glycerol using TBA has been patented. [24]

The flow diagram of reactive distillation is shown in Figure 23.

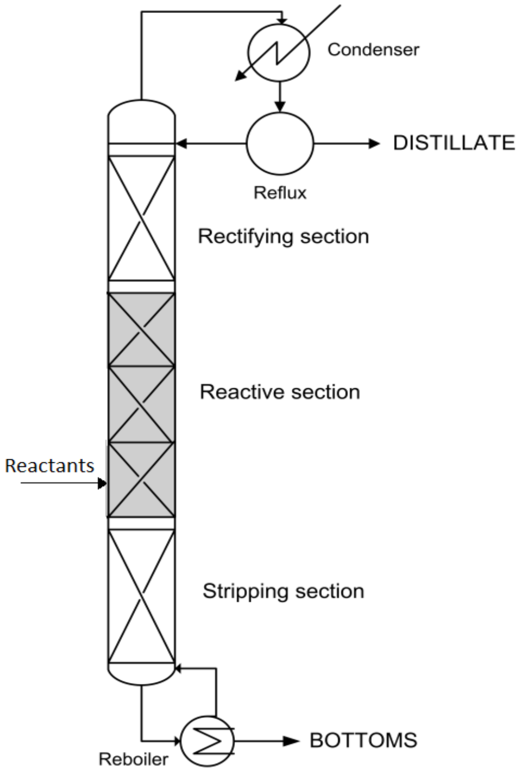


Figure 23: Concept of reactive distillation

The middle section of the column is the reactive section. For a non-azeotropic system, the separation of the inerts takes place in the rectifying section and the purification of the product takes place in the stripping section.

In this process, water is removed from the reaction section as a distillate, thereby avoiding conversion limitations by continuous removal of undesired products. Desired products are obtained as bottom products.

The reactive section part contains both the catalyst contact device and the distillation device. First, the reaction occurs when reactants make contact with the catalysts. Next, the reacting phase passes through the distillation device, where contact between gas/liquid is established, to obtain separation. A stripping section is placed below the reactive section, depending upon the desired purity of the product.

The use of reactive distillation for the etherification of glycerol can offer many advantages:

- two steps can be carried out in one device. This reduces the costs in pumps, piping and instruments;
- shift of the equilibrium is generated due to the vaporization of products;
- if the reaction zone is placed above the feed point, poisoning of the catalyst can be avoided. [24]

A simulation was conducted by Kiatkittipong [20] and demonstrated that a suitable configuration for RD consists of 6 rectifying stages and 6 reaction stages, without stripping stage.

An economic evaluation of the process was performed for reactive distillation, the total annual energy cost would be $33 \cdot 10^3$ $/year [26] which is significantly lower than the earlier mentioned 1178 000 $/year for the traditional design.

ARCO-process

In the ARCO-process, the reaction of glycerol with isobutene is carried out in the liquid phase in a two-phase reaction system, employing an acidic catalyst.
One phase is the polar, glycerol-rich phase that contains the catalysts and is conveniently recycled. The other phase is an olefin-rich apolar hydrocarbon phase (isobutene), from which product ethers can be readily separated [27].

The reaction mainly occurs in the polar phase, maintained by the mass transfer of isobutene from the apolar phase to the glycerol phase. m-GTBE will mainly remain in the glycerol phase while d-GTBE will transfer to the isobutene phase. This prevents d-GTBE from reacting to t-GTBE, being an undesirable product.

Decantation ensures the separation of the two layers. The glycerol phase is recycled back to the reaction zone, together with new glycerol and makeup catalyst. The isobutene phase is sent to a stripping column, wherein unreacted isobutene is stripped. This passes back to the reactor, also with new feed isobutene.
The bottom stream of the stripper, containing small amounts of catalyst, glycerol and m-GTBE together with large amounts of d-GTBE and t-GTBE, is washed with water to extract the glycerol, catalyst and m-GTBE. This stream can be recovered after water removal. Products di-GTBE and tri-GTBE are now available.

An advantage of this process is that it avoids the necessary separation of glycerol and glycerol ethers, which is difficult. In addition, m-GTBE, which is undesirable in this process, is returned to the reactor where it can react to form di- and tri-GTBE [27].

Behr und Obendorf process

Another process was developed by Behr and Obendorf in 2002, also using a reactor, extraction column and a flash column. [28] The process chart is displayed in Figure 24. Corresponding process conditions are displayed in Table 5. [13]

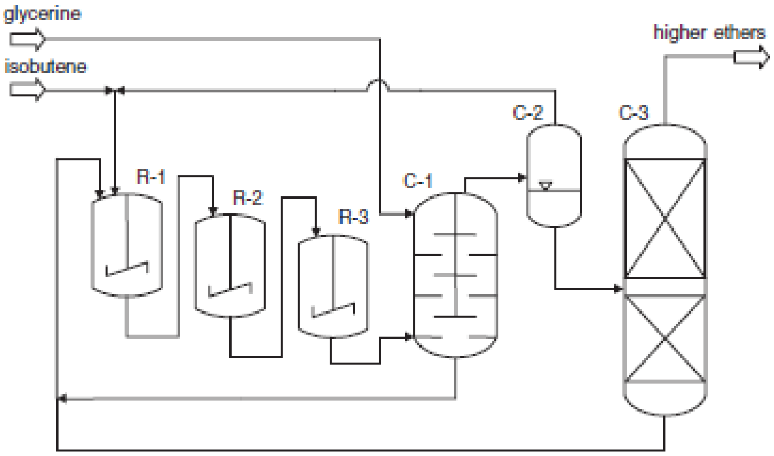


Figure 24: Behr and Obendorf design for etherification process [28]

Table 5: Conditions for the Behr and Obendorf process

Process	Temperature (°C)	Pressure (bar)
Reactor	70-110	20–30
Extraction	30-40	20-30
Flash	30-40	1
Rectification	75	0.005

In this process, isobutene is fed to the reactor while glycerol is fed directly to the extraction column. The added glycerol extracts m-GTBE and catalyst from the reaction product and is then led back to the reactor. The raffinate of the extraction is stripped in a flash column, to recover the unreacted isobutene. The last step in the process is a vacuum rectification column, to isolate pure higher ethers. This vacuum is necessary to avoid high temperatures that could cause the cleavage of the ethers, due to the presence of small amounts of catalyst.

New process based on the extraction of GTBE with biodiesel:

A new process was proposed for the production of GTBE with glycerol and isobutene.
To separate GTBE from the reaction mixture, an extraction with biodiesel is carried out. Figure 25 shows a simplified flow sheet of the GTBE-process and Table 6 shows the composition of the streams [29].

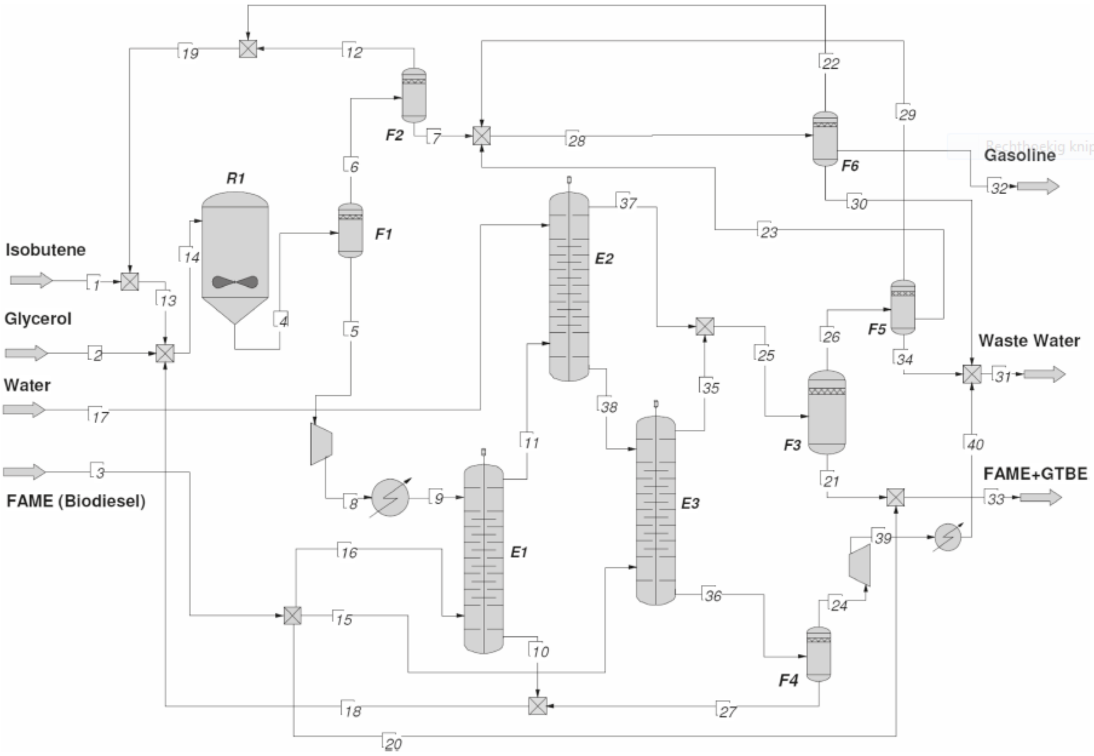


Figure 25: Process flow sheet extraction with biodiesel [29]

Table 6: Composition of the streams in figure 18 [29]

stream number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
stream name	isobutene	glycerol	FAME				gasoline										FAME + GTBE
temperature (°C)	90	90	25	90	73	73	25	73	25	25	25	25	103	15	25	25	25
pressure (bar)	20	20	1	20	0.1	0.1	1	1	1	1	1	1	20	1	1	1	1
vapor mass fraction	0	0	0	0	0	1	0	0	0	0	0	1	0	0	0	0	0
total (kg/h)	550	500	12400	1386	1225	161	38	1225	1225	212	9073	123	673	1385	4340	8060	13413
								Component Mass %									
isobutene	100			9.48	0.59	77.11	18.35	0.59	0.59	0.00	0.08	94.97	99.08	48.16			0.05
glycerol		100		8.59	9.71	0.03	0.12	9.71	9.71	50.17	0.14	0.00	0.00	43.77			0.09
mono-ether glycerol				31.72	35.89	0.02	0.07	35.89	35.89	49.13	3.70	0.00	0.00	7.52			2.50
di-ether glycerol				40.68	46.02	0.05	0.21	46.02	46.02	0.60	6.20	0.00	0.00	0.09			4.19
tri-ether glycerol				5.22	5.91	0.01	0.05	5.91	5.91	0.00	0.80	0.00	0.00	0.00			0.54
1-di-isobutylene				1.94	0.29	14.52	45.90	0.29	0.29	0.00	0.04	4.98	0.91	0.44			0.03
tri-isobutylene				2.36	1.58	8.27	35.31	1.58	1.58	0.00	0.21	0.05	0.01	0.00			0.14
methyl oleate			100	0.02	0.02	0.00	0.00	0.02	0.02	0.10	88.84	0.00	0.00	0.02	100	100	92.45

Before the extraction, hydrocarbons are removed using a flash unit, operating at 73 °C and 0,1 bar. Only the soluble amount of ethers is extracted by the biodiesel, which excludes the mono-ethers. The raffinate is recycled back to the reactor. After the extraction, the biodiesel-GTBE mixture is washed with water, to diminish glycerol content. This mixture can now be used directly as a diesel additive [29].

2.4 Gasoline/Diesel adding

A fuel additive is added to the fuel to attain certain properties and to improve the quality of the base fuel.

2.4.1 Gasoline

Motor

To understand the type of additives and their role played in the combustion chamber, it is essential to understand the types of engines and fuels. There are two types of internal combustion engines: the spark ignition engine and the Diesel engine [15].

First, fuel is diluted with air in an electronically controlled fuel injection system and throttled into the cylinder. The cycle of a spark ignition engine is carried out in a sequence of four steps:

1) intake,
2) compression,
3) ignition,
4) exhaust.

This sequence is depicted in Figure 26.

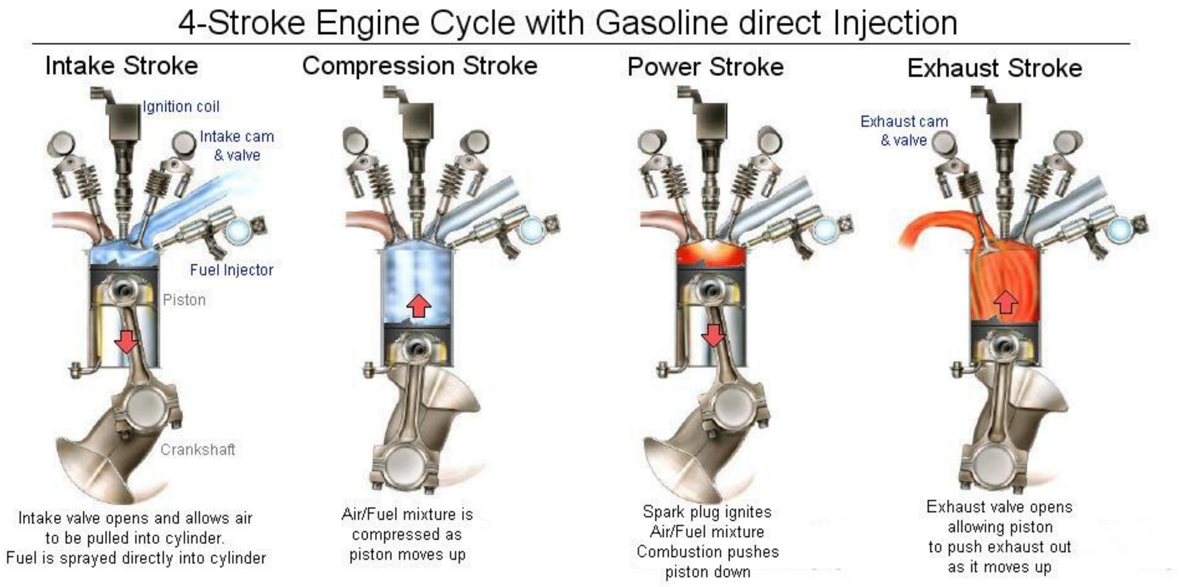


Figure 26: Schematic representation of a four stroke gasoline engine [30]

The greater the compression rate in step 2, the greater the efficiency of the engine. However, the compression rate is limited by the octane number of the base fuel. Because low quality octane fuels cause a loss in engine efficiency, octane enhancers are added to improve the octane number, enhance the engine efficiency and to avoid knocking.

Engine knocking or pinging occurs when a part of the fuel/air mixture starts to ignite spontaneously, causing the fuel to burn very rapidly and the pressure to rise very suddenly. This causes a metallic knocking sound, hence it is called “knocking” [30].

Composition

Forty years ago, it was relatively simple to produce gasoline: only specifications for octane number and volatility were required. Volatility is important because the fuel has to vaporize during cold weather, otherwise the engine won't start. If the volatility was too low, some butane could be added. If the octane number was too low, some tetra-ethyl lead could fix the problem [31].

Since the U.S. Clean Air Act, the process became more complex since tetra-ethyl lead was phased out. In 1990, limits on emission were imposed and reformulated gasoline was required. This includes a minimal amount of bounded oxygen, upper limits on vapor pressure, a 15 % reduction in volatile organic compounds.
Oxygen can be supplied by alcohols (mainly ethanol) or ethers (mainly C5-C7). Ethers have a high blending octane number and also low vapor pressure [31].

Recently, the European Parliament and the U.S. Environmental Protection Agency introduced new regulations regarding clean fuel, which demand a lower sulfur content. Sulfur can be removed by hydrotreating or selective adsorption [31].

Gasoline is a refined petroleum product and consists of a mixture of hydrocarbons, additives and blending agents. It has a boiling range from 40 °C until 150 °C. Typically, gasoline is composed of 35-64 % alkanes and alkenes, 20-50% total aromatics, including 0.5-2.5% benzene. Additives and blending agents are added. These compounds include anti-knock agents, anti-oxidants, metal deactivators, lead scavengers, anti-rust agents, anti-icing agents, upper-cylinder lubricants, detergents,… [32]
Product specifications for gasoline are described in ASTM D4814 [33].

In a refinery, several processes are performed to obtain the desired quality and type of fuel. A simplified layout for a high-conversion refinery is shown in Figure 27.

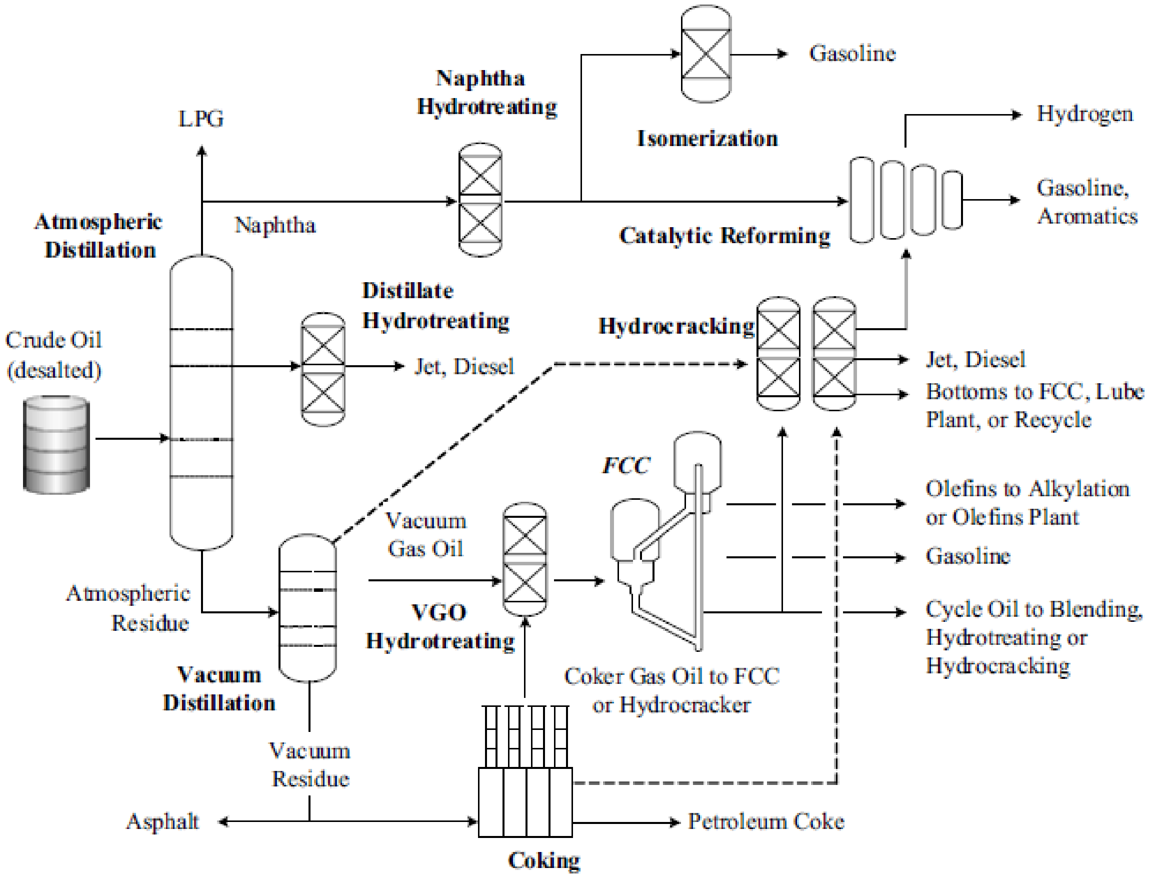


Figure 27: Simplified lay-out for high-conversion refinery [34]

First, crude oil is desalted, to reduce corrosion and to prevent catalyst poisoning. Desalting is followed by a normal distillation. Top products are LPG, propane and light naphtha. The bottom products include heavy fuel oil and asphalt residue. This stream is sent to a vacuum distillation to recover light vacuum gas oil.

The increased demand for gasoline stimulates the conversion of kerosene and other heavier fractions into gasoline. This is done by a process called cracking. This means that big molecules are split into smaller molecules with lower boiling points and lower densities. Typical cracking processes are fluid catalytic cracking (FCC), thermal cracking and hydrotreating [34]. Many FCC units are designed to process vacuum residue too (RFCC).

At the end of the production process, finished gasoline typically contains more than 150 separate compounds. [32]

Octane number

A fuel’s octane number is a measure of its ability to resist ‘knocking’. This number is calculated using a comparative scale where n-heptane has an octane number of 0 and iso-octane (2,2,4-trimethyl pentane) has an octane number of 100. The basic idea is that the combustion of the gasoline in the engine must proceed in a controlled way, to avoid knocking. When iso-octane is used as a fuel, ideal conditions are achieved. In contrast, when n-heptane is used, a pre-flame reaction is initiated and knocking occurs [35].

The octane number is determined in a test engine according to ASTM D2700. The knocking characteristics are measured against a mixture of iso-octane and heptane, with a varying composition until the qualities of knocking resistance are equal.

The octane requirement of an engine varies with compression ratio, geometrical and mechanical considerations and operating conditions. The higher the octane number the greater the fuel's resistance to knocking or pinging during combustion.

Octane number measurements can be determined in two different ways: motor octane number (MON) and research octane number (RON). The first measurement is performed under mild conditions (ASTM D 2699) and is the common used number, the latter is determined at higher mechanical and thermal loads.
The difference between RON and MON is called the sensitivity. Fuels with lower sensitivity are desired. [35]

Octane enhancers

Since 1923, tetra-ethyl lead was added to gasoline to improve its anti-knocking properties. However, a phase-out was established around 1995 (except for some developing countries who still use leaded gasoline) because of the extreme toxicity. Ever since, other compounds are developed to enhance the octane number. [36]

Octane enhancers boost the octane number and are added to the base fuel to promote cleaner fuel combustion. Due to lead pollution and toxicity, tetra ethyl lead is replaced by methyl tert. butyl ether (MTBE), ethyl tert. butyl ether (ETBE), tert. amyl ether (TAME), di-isopropyl ether (DIPE), isopropyl alcohol (IPA), isobutyl alcohol (IBA) and tert. butyl alcohol (TBA). The structures of these octane enhancers are shown below in Figure 28.

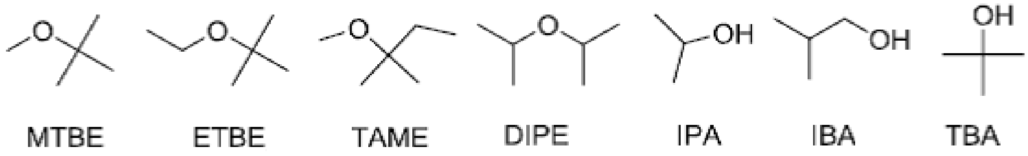


Figure 28: Oxygenates

Property measurements

Many ASTM's have been written on the properties and measurement of properties of gasoline. A short summary of some of the most important characteristics is included in this section.

- Vapor pressure: measurement of the volatility of gasoline, can be performed with ASTM D323 (Reid vapor pressure) or D4953. This property gives an idea of the gasoline performance in warm or cold conditions;
- Viscosity: measures the fluids' resistance to flow, can be carried out according to ASTM D445;
- Density: density is measured in terms of API gravity, according to ASTM D1298.
- Oxygen content: this measurement is described in ASTM D4815 and is applicable for all gasoline that contain ethers or alcohols. The oxygen content is bound to upper and lower limits by law.

Governmental laws prescribe requirements that gasoline and all other fuels have to meet. Some regulations are included in Table 7.

Table 7: Regulations European Union for gasoline [37]

		Unit	Minimum	Maximum	Testmethod	
Research octane number	RON		95	98	EN ISO	5164
Motor octane number	MON		85	89	EN ISO	5163
Density at 15°C		kg/m³	743	756	EN ISO	12185
Vapor Pressure	(DVPE)	kPa	56	60	EN	13016-1
Water content				0,05	EN	12937
Distillation						
	Evaporates at 70°C	vol%	34	46	EN ISO	3405
	Evaporates at 100°C	vol%	54	62	EN ISO	3405
	Evaporates at 150°C	vol%	86	94	EN ISO	3405
	End boiling point	°C	170	195	EN ISO	3405
	Residu	vol%		2	EN ISO	3405
Hydrocarbon analysis	Alkens	vol%	6	13	EN	22854
	Aromatics	vol%	25	32	EN	22854
	Benzene	vol%		1	EN	22854 / 238
Sulfur content		mg/kg		10	EN ISO	20846
Lead content		mg/l		5	EN	237
Ethanol		vol%	9	10	EN	22854

As can be seen from Table 7, density and vapor pressure are restricted. Later in this thesis, these characteristics will be tested and compared to these requirements.

2.4.2 Diesel

Motor

The main difference between gasoline motors and diesel motors is the ignition source. Diesel fuel has to auto ignite under pressure and therefore no ignition source is needed. The cycle of a diesel engine also consists of 4 steps:

1) intake,
2) compression,
3) auto ignition,
4) exhaust.

These 4 steps are displayed in Figure 29: Diesel engine

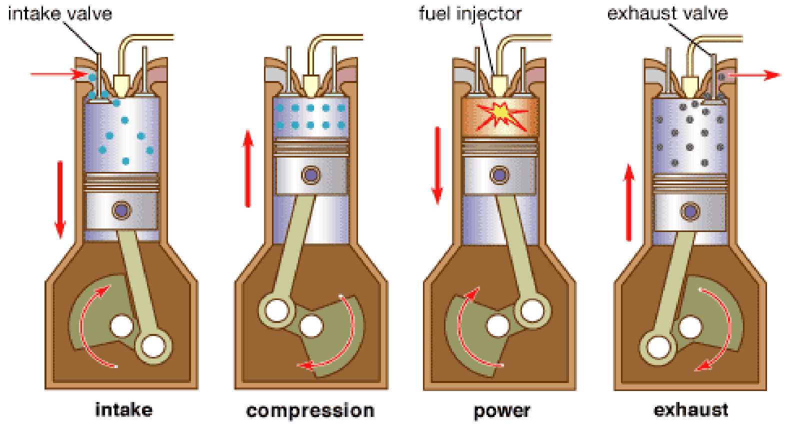


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Figure 29: Diesel engine

Air is taken into the cylinder unthrottled and compressed to obtain a pressure of 30 to 55 bars, which generates temperatures up to 700 °C. Fuel is injected into the heated air shortly before the end of the compression stroke.

Composition

Diesel consists of hydrocarbons mainly in the range of C9-C20 and a boiling range from 163 °C up to 357 °C. [38] Diesel nowadays, must be free of sulfur.

Diesel fuels are remarkably less volatile than gasoline. They are classed as middle distillates and are denser than gasoline, thus providing more energy per unit volume than gasoline.

Cetane number

In contrast to gasoline, diesel fuel must auto ignite. The cetane number gives an indication of the ignition quality of a diesel fuel, it gives no indication of the fuel quality. More precisely, cetane number is a measure for the ignition delay, this is the time between the compression and start of combustion. A high cetane number means easy combustion. [15]
The most common used cetane enhancers are nitrates and peroxides. A commonly used additive is 2-ethylhexyl nitrate, displayed in Figure 30.

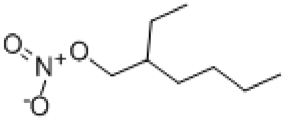

Figure 30: Additive 2-ethylhexyl nitrate [15]

2.4.3 Emissions and pollution

In an internal combustion engine with ideal conditions, following reaction would occur:

$C_mH_n + (m + 0,25n)\ O_2 + p\ N_2 \rightarrow m\ CO_2 + 0,5n\ H_2O + \text{heat} + p\ N_2$

Unfortunately, it is impossible to achieve ideal conditions, even in technologically most modern engines. Due to a lack of homogeneous gas phase and chemical equilibrium, several undesired compounds are formed and the following general reaction occurs:

$a\ C_mH_n + b\ O_2 + c\ N_2 \rightarrow d\ CO_2 + e\ H_2O + \text{heat} + f\ N_2 + g\ C_qH_r + h\ NOx + i\ CO$

Unideal conditions lead to an incomplete combustion, creating carbon monoxide (CO).
Under high pressure and temperatures, nitrogen and oxygen atoms in air can react and form nitrogen oxides, so called NOx.
Another category of emissions is caused by the hydrocarbons. Hydrocarbon emissions result when fuel molecules in the engine do not burn or burn only partially.

Hydrocarbons and NOx are precursors for the formation of ozone and also contribute to the formation of acid rain [1].

Particulate matter is a last group of emissions. It is a cluster of solid or liquid particles that are emitted from the exhaust. Particulate matter ranging from 2.5-10 microns can enter the human body and are considered dangerous.

Diesel engines, in comparison with gasoline engines emit less carbon monoxide (CO) but over 20 times more nitrogen oxides (NOx). This could be solved by selective non-catalytic reduction, however, regulations still have to be worked out. Diesel engines contribute to most of the particulate matter pollution.

2.4.4 Oxygenates

General

Fuel oxygenates are oxygen rich compounds (mostly alcohols, ethers) added to the fuel to improve combustion and fuel properties. Tests have shown that 2 % oxygen results in a 9 % decrease of CO emissions [39]. In addition, they generally have a lower volumetric energy content than gasoline and thereby reduce the energy content of the blend, when blended with gasoline. This reduction benefits the car's fuel economy for 1-3% [40]. For the moment TBA and bio-ethanol are the most used oxygenates. MTBE was a common used oxygenate, invented to replace tetra-ethyl lead. However, since early 2000 it was detected in the ground water of the USA and forbidden. Ever since, the methanol group in MTBE has simply been replaced by an ethanol group [41]. A survey of some of the most commonly used oxygenates together with their physical properties is given in Table 8.

Table 8: Physical properties of commonly used oxygenates [40]

Oxygenate	Blending Octane (R+M)/2	Blending Reid Vapor Pressure (psi)	Boiling point (F)	Energy content (MBTU/gal)	Oxygen Content (%)	Water solubility (%)
Ether						
MTBE	110	8	131	93.5	18,2	4,3
TAME	105	2.5	187	100.6	15.7	2
ETBE	112	4	161	96.9	15.7	1.2
IPTBE	113	2.5	188	Not Available	13.8	Not available
TAEE	100	1	214	Not Available	13.8	Not available
DIPE	105	5	155	100	15.7	2
Alcohol						
Ethanol	115	18	173	76	34.8	Infinite
TBA	100	9	181	94.1	21.6	Infinite
Iso-propanol	106	14	180	87.4	26.7	Infinite
Iso-butanol	102	5	226	95.1	21.6	10
Tert-Amyl Alcohol	97	6	216	100.1	18.2	11.5

Oxygenates preferably show a high blending octane number and high oxygen content. When looking at the boiling point, additives can be used for refineries to meet the distillation temperature requirements.

Oxygenates in diesel fuel are mainly added to reduce the particulate matter exhaust while oxygenates in gasoline are added to enhance the octane number.

To give an idea of the percentage of additive in fuel: ETBE is widely used as gasoline additive to reduce emissions of CO and unburned hydrocarbons. In Japan, regulations require that the mass fraction of ETBE in gasoline must be kept within 1.3 m% and 8.3 m%. [42]
In the USA, the levels that can be added are controlled by the Clean Air Act amendments.
Europe too sets environmental specifications for market fuels. The maximal allowed oxygen content in gasoline is 2.7 m/m % (measurements carried out according to EN 1601).

For quality control and regulatory purposes, the monitoring of individual oxygenates in gasoline is important. Oxygenates can be determined using gas chromatography, molecular spectroscopy, infrared spectroscopy, NMR,... [43]

Blending process

The application of modeling systems based on adequate mathematical models can provide the most appropriate and precise blending recipes for optimal blending. Examples are Aspen Process Industry Modeling System and Blend Optimization and Supervisory System (BOSS).

The octane number of gasoline blends deviates from the law of additivity: differences in the properties of individual compounds in a free condition and in mixtures with other hydrocarbons take place in every hydrocarbon stream [44]. They obey Raoult's law closely enough to estimate vapor pressure but not closely enough to predict or simulate distillation and octane number. Therefore a blending octane number has to be calculated. [45] This number can be calculated using several models which take into account the several intermolecular interactions [45].

GTBE as oxygenate

Glycerol tert. butyl ethers contain oxygen, which makes them usable as oxygenate. Since GTBE is a mixture of 5 different ethers, with different characteristics, one should favor the formation of the desired product(s) to use the mixture as oxygenate.

m-GTBE shows different characteristics than di- and tri-ethers, the so called higher ethers. Higher ethers are less polar than mono-ethers and show a good solubility in diesel fuel and gasoline. Moreover, the density of di- and tri-ethers is higher. These properties make higher ethers perfect substitutes for the current used oxygenates.

If the purpose is to use GTBE as oxygenate for diesel fuel, the amount of m-GTBE has to be minimized. The main effects of the addition to diesel fuel are the reduction of unburnt compounds and the suppression of soot emission [46].

Mono-ethers are more polar and therefore, show a low solubility in water, which makes them undesired as an additive in diesel fuel.
However, due to their lower density, mono-ethers can be blended with gasoline.
The octane number for m-GTBE is higher than the octane number of the higher ethers, offering a possibility for an even more efficient oxygenate.
These mono-ethers show properties that are very similar to MTBE, which is banned in the USA, for the possible danger they might form to ground water [28].

Influence of GTBE oxygenate on fuel

The influence of GTBE on fuel is investigated by several authors [23] [42] [46]. The main impacts can be summarized as follows:

- oxygenates lower the content of particulate exhaust and unburnt gaseous emissions without significant impact on combustion processes [46];
- the fuel conversion efficiency is enhanced due to the beneficial effect of intra-molecular oxygen [46] ;
- a reduction in cloud point and viscosity can be observed [25] [23];
- a decrease of vapor pressure is achieved [23].

3 Materials and methods

In this section of the thesis, essential information is given about the used materials and followed procedures for the carried out experiments.

3.1 Chemicals

Anhydrous glycerol (purity of 99%), supplied by Xilong Chemicals, and tert. butyl alcohol (purity of 95%), provided by Sage Chemicals, were used as reactants.

Beta Zeolite was employed as a catalyst.
Beta Zeolite (Zeolyst international) is a water free crystalline aluminosilicate and is baked in the oven for five hours in air of 450°C before use, to activate the catalyst. [47]
The specifications of Beta Zeolite can be found in attachment nr. 2.

For analysis, acetonitrile reagent-grade, provided by Xilong Chemicals, was used as a solvent. Di-ethylene glycol mono-butyl ether (purity of 99%), supplied by Merck, served as the internal standard in the chromatographic analysis.

Dung Quat refinery provided three types of gasoline to blend with the m-GTBE: motor gasoline with an octane number of 92 (mogas 92), gasoline after normal distillation (NDC gasoline) and gasoline after residue fluid catalytic cracking (RFCC gasoline).

3.2 Characterization of Beta Zeolite

The exact conditions, equipment and procedures for the characterization of Beta Zeolite can be found in the thesis of Simon Scholtz [48], who characterized the catalyst and whose results are used for this thesis.
The conducted tests included X-ray diffraction (XRD), Fourier Transform Infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and physical adsorption with N_2 (BET).

X-ray diffraction can be used to determine the crystallinity of the catalyst, by checking the intensity of the characteristic beta zeolite peaks. The higher the peak area, the higher the crystallinity and the better the catalyst.
Fourier Transform Infrared spectroscopy characterizes the molecules in the catalyst, by checking transmittance as function of the wavenumber.
Scanning electron microscopy indicates the catalysts' morphology and crystal size. The surface area and pore size can be measured with N_2 adsorption and use of the Brunauer Emmett and Teller theory (BET). The higher the surface area and porosity, the higher the efficient total reaction area for the catalyst [48] [49].

3.3 Etherification of glycerol with tert. butyl alcohol

Etherification reactions were carried out with a laboratory autoclave reactor (capacity: 500 ml.) that was equipped with an anchor type electric stirrer. The reactor and stirrer were supplied by Parr. The autoclave is visualized in Figure 31.

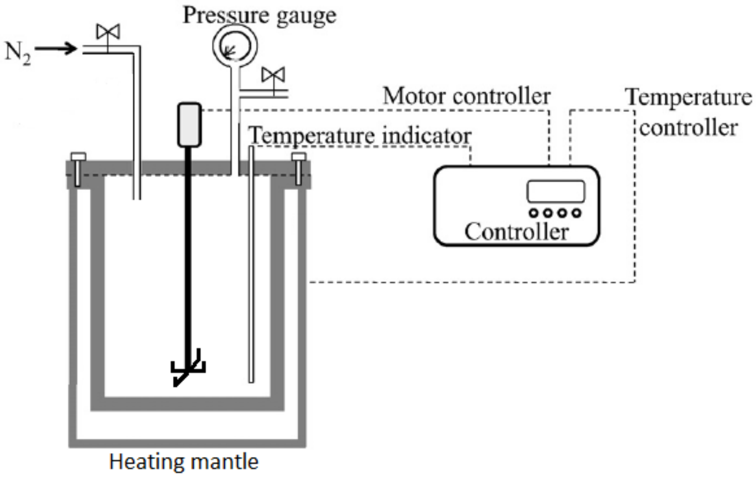

Figure 31: Autoclave reactor for etherification of glycerol with TBA

The reactor temperature and the stirring rate were controlled by a PARR controller type 4843. Pressure was held constant at 10 atm. using N_2-gas.

In a typical run, 20 ml of glycerol was used. The amount of tert. butyl alcohol was determined by a molarloadingof Glycerol/TBA: 1/4.
When TBA was added to the glycerol, a magnetic stirrer was used to homogeneously mix the reactants for 15 minutes. Afterwards, a 1.0 ml sample was taken for analysis with GC-MS.

For determining the optimal conditions, a 2^3 experiment was composed, using the technique of Design of Experiments. The three process variables or chosen design parameters were temperature, reaction time and catalyst loading with respect to glycerol mass. The responses were the yield, the conversion and the selectivity. The levels for the parameters were chosen carefully after a literature review [5]. Further specifications of this design are given under 3.6 and 4.5.

In Figure 32, a flow chart of the process can be found.

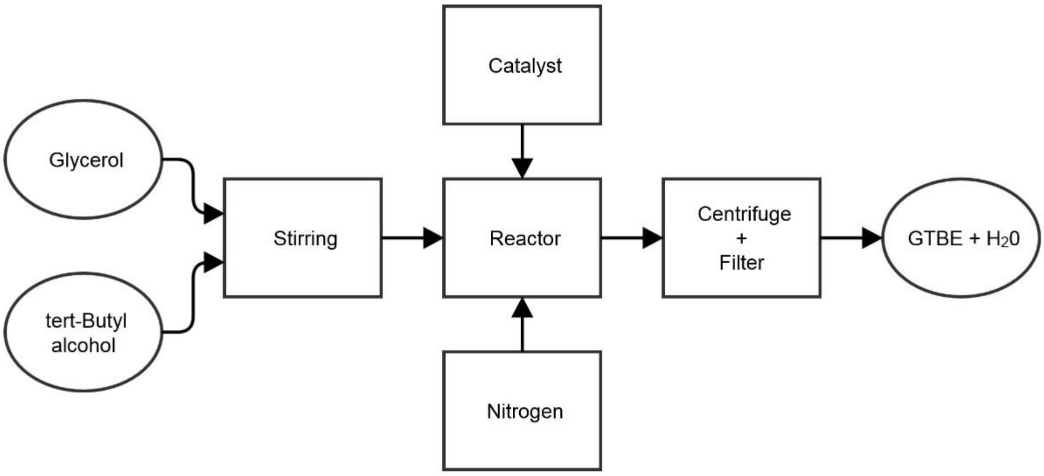

Figure 32: Process: etherification of Glycerol

To start the reaction, catalyst was placed into the reactor, followed by the mixture of glycerol and TBA. The autoclave reactor was sealed, pressurized and heated.

After the scheduled time for reaction, the autoclave is cooled by water until 25°C and the reactor is slowly depressurized. Catalyst and products are separated using a centrifuge (Rotina 15) for 15 min. at 1500 rpm. During the centrifugation, the cup is sealed to prevent tert. butyl alcohol from evaporating.
After centrifugation, the mixture is filtered to eliminate the catalyst. The final product is stored in a dark glass bottle while the catalyst is recovered.

The final products from these reactions were collected and are used to isolate the mono-GTBE. A 1.0 ml sample from every reaction product was taken and analyzed with GC-MS to determine the conversion, selectivity and the composition of the final product.

3.4 Analysis of samples using GC-MS

The samples of reactants and products were analyzed by a Finnigan Trace GC-MS Ultra. The analyses were carried out on a capillary column TRACE Rtx with Wax GC Columns (30m x 0.25mm x 0.25µm). The temperature program started at a temperature of 60°C, followed by an isothermal period of 5 minutes. Then, the temperature increased with 10°C per minute until the final temperature of 220°C was reached, at which it was held for 5 minutes.

To determine the concentration of the different compounds in the samples, standard lines of glycerol, tert. butyl alcohol and m-GTBE were composed. The procedures for setting up these standard lines were very similar: first, a specific amount of the component was weighed and added to a 25.0 ml flask (1000 µl for tert.butyl alcohol, 250 µl for glycerol and 50 µl for m-GTBE).
Then, the chemical was diluted with acetonitrile up to 25.0 ml, except for m-GTBE which is diluted to 4.0 ml instead of 25.0 ml.
After shaking this 25.0 ml mixture for 1 minute, it can be used to prepare five different concentrations.
50, 100, 200, 400 and 800 µl respectively was added to five 5 ml vials. These vials were diluted with acetonitrile up to 1.0 ml and finally, 20 µl of internal standard was added.

Afterwards, the vials were analyzed and the ratio of peak area of the chemical to the peak area of the internal standard was used to compose the standard line.

For the analysis of reagents and products, 1.0 ml of reagent or product was added to a vial, together with 20 µl of internal standard. The concentration of reagent or product can be calculated using the standard lines and the area ratio.

3.5 Statistical validation

Before any experimental value can be used to draw conclusions, a statistical validation has to be carried out to ensure representative values and correct measurements.

3.5.1 Reproducibility

The reproducibility was calculated as standard deviation, using the three centerpoints. The standard deviation can be calculated as follows:

$$s = \sqrt{\frac{\sum(x - \bar{x})^2}{n - 1}}$$

3.6 Optimization of etherification of glycerol

The optimal reaction conditions were defined to be those conditions that give the highest yield of m-GTBE, combining a high conversion of glycerol with a high selectivity for m-GTBE. The optimal conditions were calculated with the theory of Design of Experiments and were simulated afterwards. A 2^3 full factorial design was set up with 3 center points. The three factors were temperature, reaction time and catalyst loading. The molar ratio TBA/Gly was set at 4/1 for all experiments. The responses were conversion of glycerol, selectivity for m-GTBE and the yield.

The levels for the factors were chosen after literature review and are mentioned below in Table 9.

Table 9: Factor levels for a 2^3 Design

Factor	Low level (-1)	Center point (0)	High level (1)
Temperature (°C)	80	95	110
Reaction time (h)	2	4	6
Catalyst loading with respect to glycerol mass(wt%)	5	7.5	10

Table 10 gives a survey of the reactions that were carried out. It should be noted that the experiments were randomized to avoid systematical errors.

Table 10: Experiments for the 2^3Design

Temp (°C).	**Reaction time (h)**	**Catalyst loading (wt% with respect to glycerol mass)**
80	2	5.00
80	6	10.00
95	4	7.50
80	2	10.00
95	4	7.50
80	6	5.00
110	2	10.00
110	6	5.00
110	2	5.00
95	4	7.50
110	6	10.00

The conversion of glycerol can be calculated in multiple ways. The general definition of conversion can be written as:

$$x_{Gly} = \frac{n_{0,Gly} - n_{1,Gly}}{n_{0,Gly}} \qquad (1)$$

In this formula, $n_{0,Gly}$ is the amount of moles glycerol at the start of the experiment while $n_{1,Gly}$ is the amount of moles glycerol at the time that the conversion is determined.

The analysis with GC-MS allows an easier but correct way to calculate the conversion. When working with GC-MS, an internal standard is always added, to correct for errors in injection volume. For analysis, the area of the desired peak is always referred to the peak area of the internal standard. This way, following formula can be applied for the determination of the conversion:

$$x_{Gly} = \frac{\frac{Ratio_{Gly,reagent}}{Mass_{sample,reagent}} - \frac{Ratio_{Gly,product}}{Mass_{sample,product}}}{\frac{Ratio_{Gly,reagent}}{Mass_{sample,reagent}}} \tag{2}$$

The selectivity for m-GTBE is defined as:

$$selectivity = \frac{n_{m-GTBE}}{n_{0,Gly} - n_{1,Gly}} \tag{3}$$

The amount of m-GTBE can easily be determined by using the standard line for m-GTBE and the same goes for the amounts of glycerol.

The purpose of this design of experiment was to maximize the yield of m-GTBE. The yield is defined as:

$$yield = conversion \cdot selectivity = \frac{n_{m-GTBE}}{n_{Gly,reacted}}$$

For each reaction, the conversion of glycerol and the selectivity for m-GTBE was calculated, by means of GC-MS analysis. The different spectra are included in attachment nr. 3. The yield was calculated with the results from the conversion and selectivity.

3.7 Separation of m-GTBE from reaction mixture

The produced reaction mixture contains glycerol, water, tert. butyl alcohol and m-, d-, t- GTBE. To isolate m-GTBE, multiple steps are necessary. The boiling points of the different compounds at different pressures are displayed in Table 11.

Table 11: boiling points (T_b)of compounds in GTBE mixture [25]

P (mm Hg)	T_b (°C) m-GTBE	T_b (°C) d-GTBE	T_b (°C) t-GTBE	T_b (°C) Glycerol	T_b (°C) TBA	T_b (°C) Water
760	257	240	253	288	82	100
40	160	140	150	188	10	30
80	170	145	157	205	26	44
100	180	165	172	215	35	46
200	210	190	195	235	52	63

Since TBA has a low boiling point, compared to the others, the first step was to remove TBA from the mixture.

A normal distillation is applicable for the separation of liquids that boil below 150°C and with a difference in boiling point of at least 25 °C. The liquids should dissolve in each other [50]. For these reasons, the separation of GTBE from TBA could be carried out by means of a normal distillation under atmospheric pressure. The set-up is displayed in Figure 33.

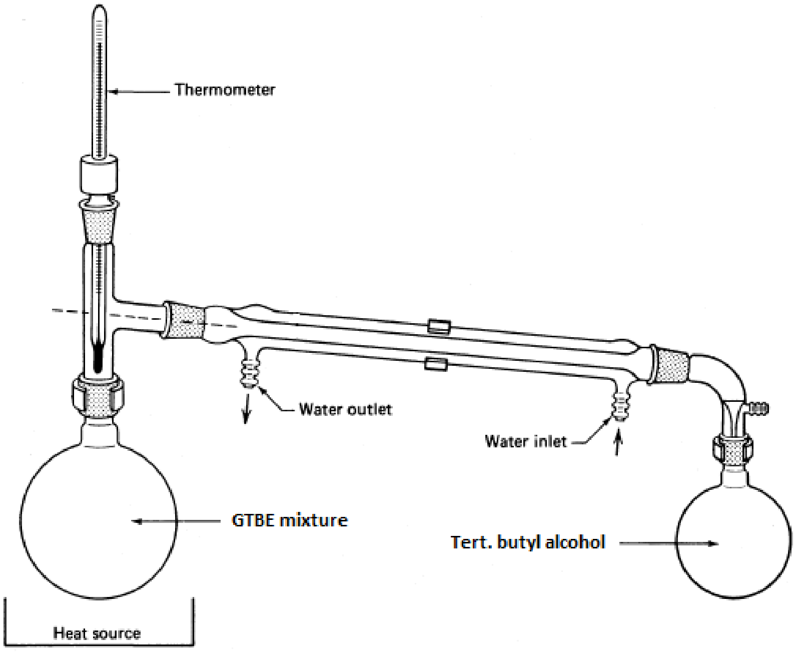

Figure 33: Normal distillation of GTBE [50]

The distilling flask was filled with 180 ml of reaction product. A heating mantle was used to provide heath and boiling stones were added to the distilling flask. If no heating mantle is available, a rotary evaporator can be used.

After distillation, GTBE (+glycerol) was left in the distilling flask while TBA (and potentially some water) was found in the receiving flask. 1.0 ml samples were collected before and after distillation to determine the separation efficiency.

Afterwards, the m-GTBE had to be isolated from the di- and tri-GTBE. This was done by means of a vacuum distillation. The set-up for vacuum distillation is shown in Figure 34.

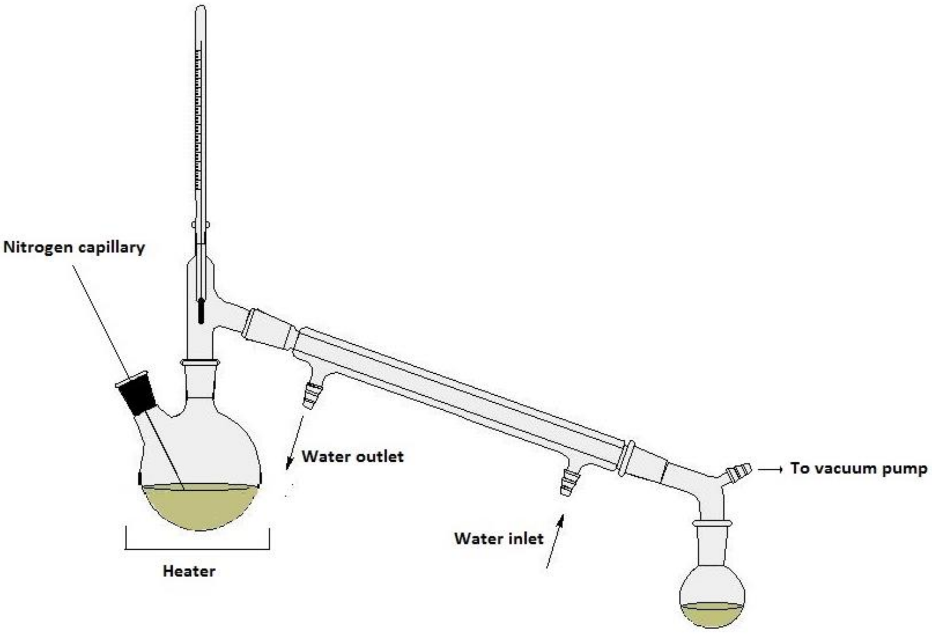

Figure 34: Vacuum distillation of GTBE

Firstly, the distillation flask was filled with 150 ml of GTBE and a vacuum of 80 mm Hg was installed. Then, the distilling flask was heated with a heater. The first fraction is a residue of TBA and water which boil first. The heater is turned off and when the system is cooled down, the pressure is changed to 40 mm Hg. The second fraction is distilled and contains d- and t-GTBE. Finally, the third fraction contains m-GTBE. To determine the separation efficiency, 1.0 ml samples were taken before and after.

To acquire a high level of purity, several distillations were necessary. The purity of the distillate was checked with GC-MS.

Another possibility to separate m-GTBE from the reaction product is to complex glycerol and m-GTBE with $Cu(OH)_2$. Afterwards, the glycerol and the m-GTBE can be separated by means of a vacuum distillation.

3.8 Blending m-GTBE with gasoline

m-GTBE was blended with the gasoline in three different quantities, 2.5 v%, 5 v% and 7.5 v%. All characteristics except octane number were determined firstly. Therefore, 300 ml blends of each concentration were prepared. To do so, respectively 7.5, 15 and 22.5 ml of m-GTBE was pipetted into a closed bottle of 500 ml. Then respectively 292.5, 285 and 277.5 ml of commercial gasoline was added. Attention had to be paid: m-GTBE is extremely hydrophilic and moisture in the air should be avoided, as well as wet equipment.

Afterwards, the bottles were shaken for 1 hour by means of a vibrational plate, IKA® HS control. The frequency was 300 vibrations/min. After this step, the m-GTBE should homogeneously be blended with the gasoline.

The next and final step was to cool down the blend for 30 minutes in an ice bath. This allows the vapor to condense and limits the loss of gasoline when opening the bottles.

3.9 Characteristics blend

Several characteristics of the three different gasoline blends were tested.
The octane number indicates the types of hydrocarbons that are present in the blend. A sample of the blend was sent to another laboratory to determine the octane number (ASTM D2699). The results of this analysis will be published later.
An Engler distillation was carried out to check the boiling range. In addition, the density, vapor pressure and oxygen content were determined. The measurements are carried out according to ASTM standards (D86, D1298, D4935 and D4815).

Afterwards, the resulting characteristics of the blended gasoline were compared to the characteristics of the pure gasoline to check the influence of mono-GTBE.

4 Results and discussion

In the previous part, all materials and methods were explained. In this section, the results will be presented and discussed. This section starts with the characterization of Beta Zeolite. Secondly, the optimization of the etherification will be carried out and finally, the influence of m-GTBE on the characteristics of pure gasoline will be discussed.

4.1 Characterization catalyst

4.1.1 X-ray diffraction (XRD)

When synthesizing a product, a check for the product has to be done to make sure the right product is synthesized. When synthesizing Beta Zeolite, this check can be done by means of XRD. Also, the crystallinity can be compared with other synthesis by comparing the intensities of the characteristic peaks.

A standard X-ray diffraction pattern for Beta Zeolite can be found in literature and is depicted in Figure 35.

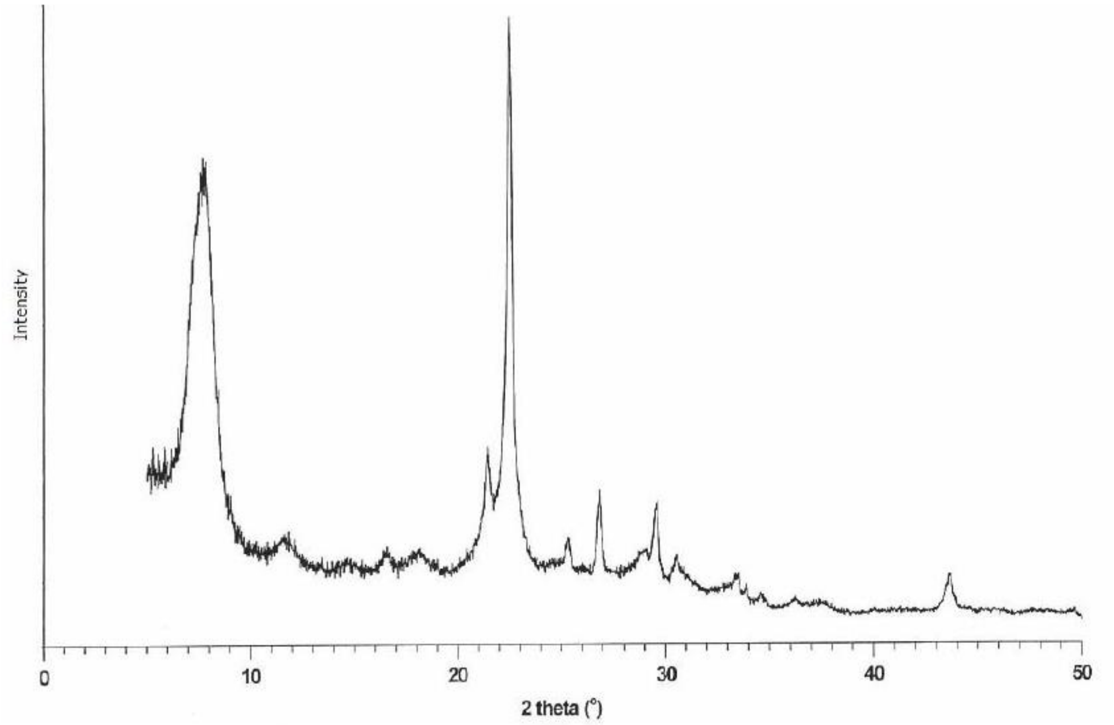

Figure 35: Standard XRD for Beta Zeolite [48]

Figure 35 reveals three characteristic 2 theta values: 7.5, 21.2 and 22.5.

An XRD was taken from commercial Beta Zeolite of Zeolyst, with a SiO_2/Al_2O_3 molar ratio of 25/1 and is depicted in Figure 36.

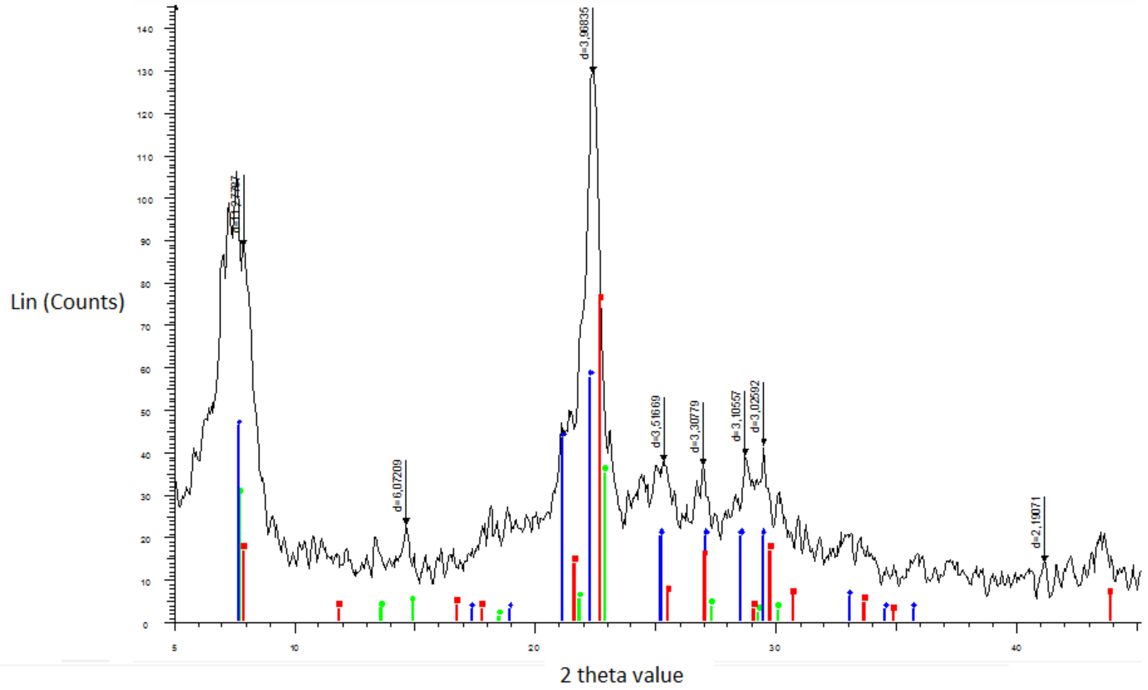

Figure 36: XRD for commercial Beta Zeolite [48]

When comparing this XRD with the standard XRD, it is easy to notice the similarities. The three characteristic peaks for Beta Zeolite are found in both XRD's and in this way, the identity of Beta Zeolite is confirmed.

4.1.2 Fourier Transform Infrared spectroscopy (FTIR)

The composition of Beta Zeolite and potential impurities can be checked with Fourier Transform Infrared spectroscopy.

The spectrum before and after calcination of the catalyst at 500 °C is shown below, in Figure 37.

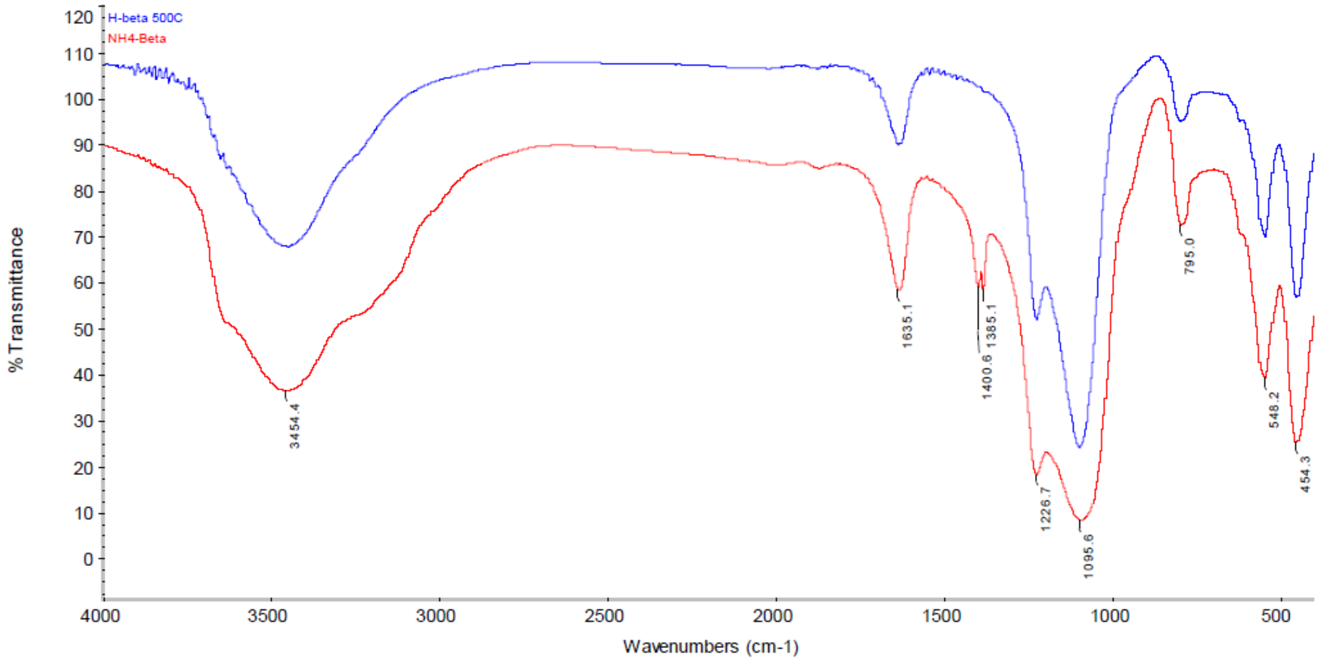

Figure 37: FTIR before (bottom line) and after (top line) activation of Beta Zeolite [48]

Both FTIR spectra show similarities as well as differences.
The peak between 3800 cm^{-1} and 3200 cm^{-1} refers to the presence of 5 different hydroxyl groups that all contribute to the large peak, being:

- Acidic bridging hydroxyl groups, at 3605 cm^{-1}. Its intensity strongly depends on the composition of the sample. These groups compensate for the negative charge of aluminum, to which they are bonded;
- Hydroxyl groups that are bonded to aluminum that is situated at the outside of the structure, from 3660 to 3680 cm^{-1}. These hydroxyl groups are stated to be nonacidic [1];
- Hydroxyl groups that are bonded to the internal silicon at framework defects, at 3730 cm^{-1}. The number of hydroxyl groups that fills the defect sites affects the thermal stability;
- Hydroxyl groups that are bonded to terminal silicon, at 3745cm^{-1}. The concentration of these hydroxyl groups is dependent on the crystal size: the smaller the particles, the more hydroxyl groups are required to close the spheres of silicon on the outer surface. Generally, beta zeolite synthesis results in small crystals and therefore, a relative intense vibration band at this wavenumber. The intensity is not influenced by activation [1].
- Hydroxyl groups that cause a very high frequency band, at 3782cm^{-1}. The appearance of this band can be associated with aluminum-containing molecules. Literature also assigns this band to terminal AlOH-groups that are bound to single aluminum [1] [1].

This big peak is the most important peak in the spectrum.

After activation, the peak at 1400-1385 cm^{-1} disappeared. This peak can indicate a C=C-bond or a CH_3-bond, both bonds leave the compound by long term heating.
The two large peaks at 1225 cm^{-1} and 1100 cm^{-1} possibly indicate Si-O or Si-C bonds [48].

The peak at 1095.6 cm^{-1} could relate to Si-OH deformation. After activation, the transmittance has decreased (thus absorption has increased).

At 1635 cm^{-1}, both spectra show a peak. This peak can be assigned to the presence of a C-C bond but it can also indicate a N-H bond. Both possibilities relate to the presence of tetra-ethyl ammonium hydroxide, which was used as templating agent. After heating, this molecule partly leaves, resulting in a decrease of absorption.

4.1.3 Scanning electron microscopy (SEM)

The morphology and particle size of Beta Zeolite were determined with scanning electron microscopy. To determine the influence of the activation, a SEM before and after activation at 450 °C were registered and shown in .

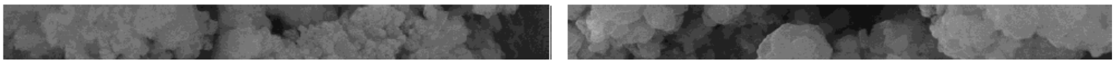

Figure 38: SEM before activation of Beta Zeolite (left) and after activation of Beta Zeolite (right) [48]

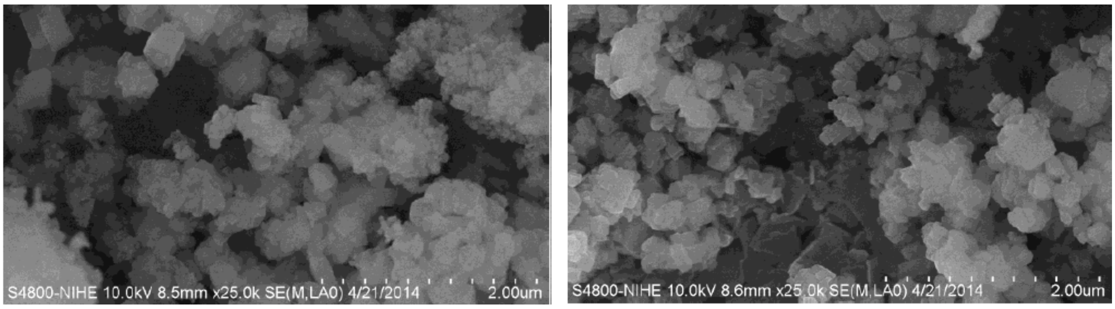

Figure 38 (left) shows the morphology of Beta Zeolite before activation. No significant difference in morphology or size is detected after activation [48]. The size is smaller than 1 µm but mostly between 0.3 and 1 µm.

4.1.4 Physical adsorption with N_2

The specific surface area and pore size of Beta Zeolite can be determined by means of the nitrogen adsorption and desorption isotherm. The specific area was calculated using both the BET theory and the Langmuir theory. The pore size was calculated by the adsorption average pore width, calculated by BET.

The total surface area was determined to be 422 m²/g, according to the BET theory. When applying the Langmuir theory, the total surface area was 527 m²/g. The pore size was 21 Å.

In Figure 39, the ad- and desorption isotherms are shown.

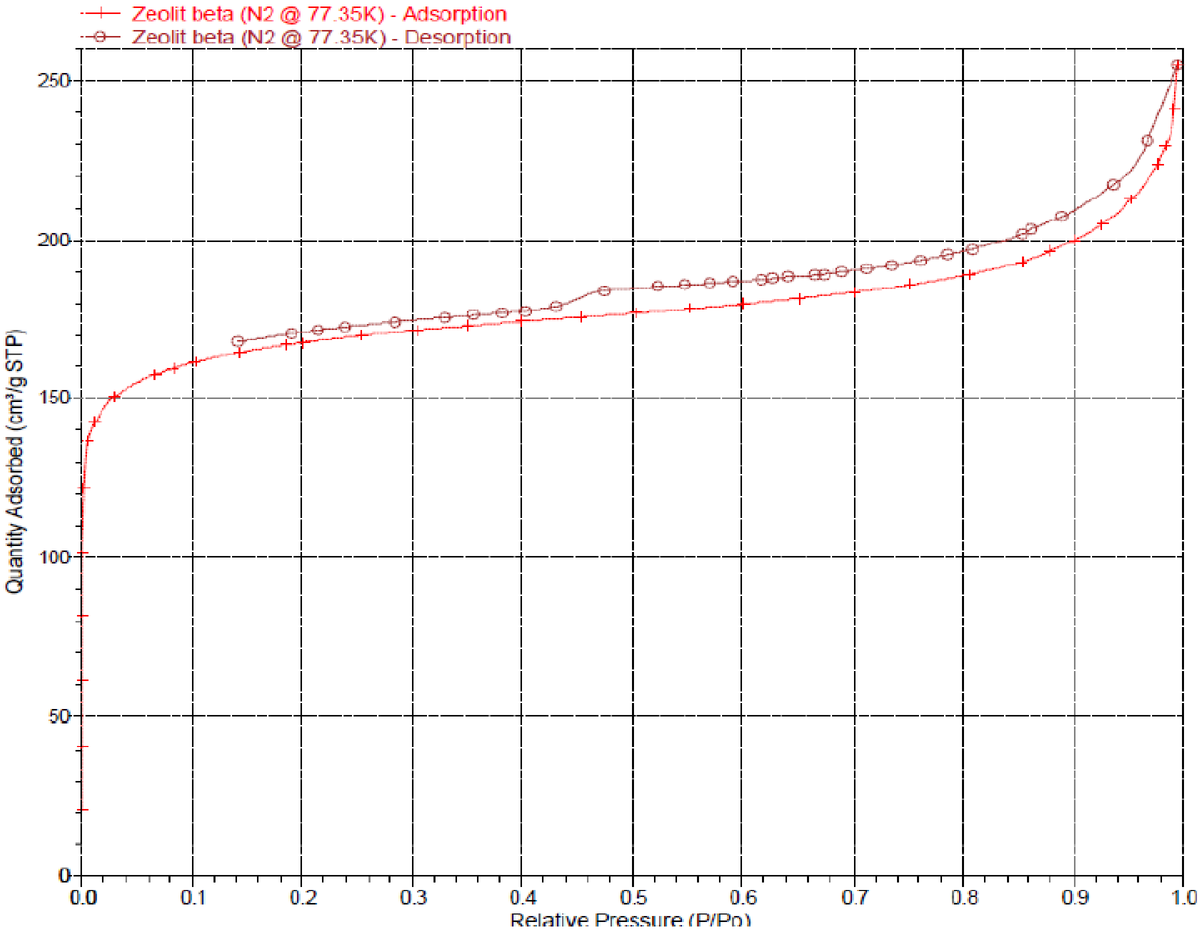

Figure 39: Adsorption and desorption isotherm at 77,35 K of Beta Zeolite [48]

According to IUPAC classification, the isotherm type is type 2. This type describes the adsorption on macroporous adsorbents with strong affinities. From the adsorption isotherm it can be concluded that multilayer adsorption occurs, after formation of the monolayer.

As a result, Beta Zeolite can be considered to be a wide pore size zeolite. The earlier analysis showed that the pore size is 21 Å, which is in the mesoporous range, according to IUPAC.

4.2 Standard lines

Standard lines play a very important role in the determination of the conversion and selectivity. Multiple standard lines are set up and compared to approve the right equation.

4.2.1 Glycerol

The standard line for glycerol is shown in Figure 40.

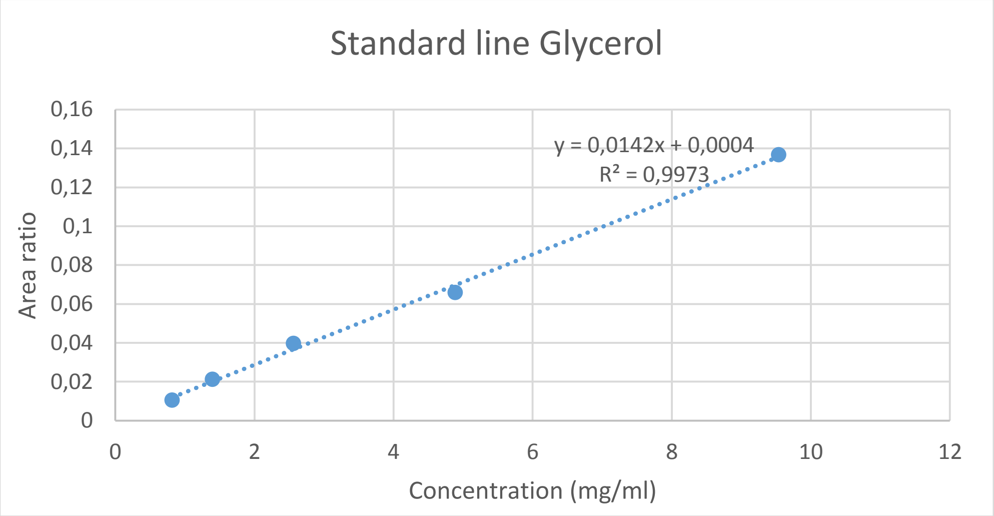

Figure 40: Standard line for glycerol

From this standard line, the concentration of glycerol in the sample can be calculated.

4.2.2 Tert. butyl alcohol

The standard line for tert. butyl alcohol is shown in Figure 41Figure 40.

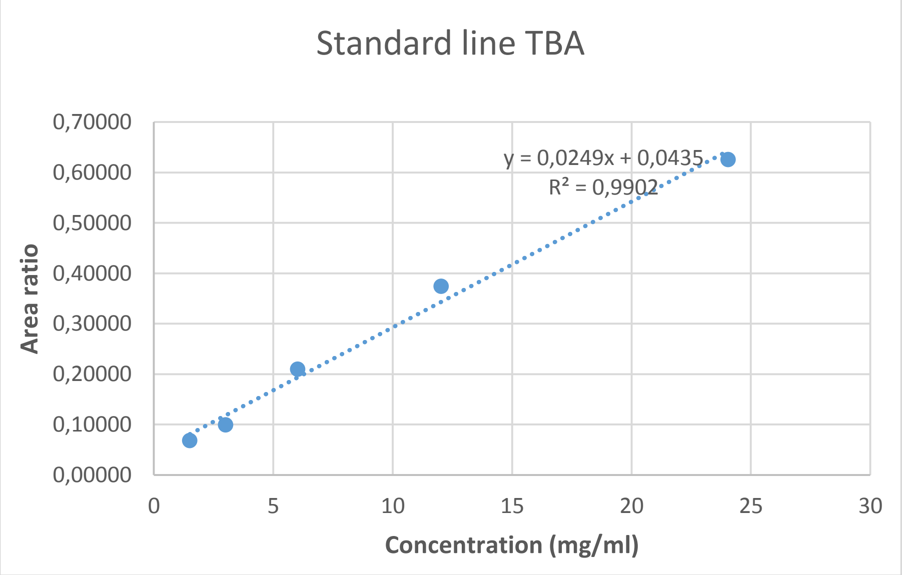

Figure 41: Standard line for TBA

From this standard line, the concentration of TBA in the sample can be calculated.

4.2.3 Mono-tert. butyl ether

The standard line for m-GTBE is shown in Figure 42.

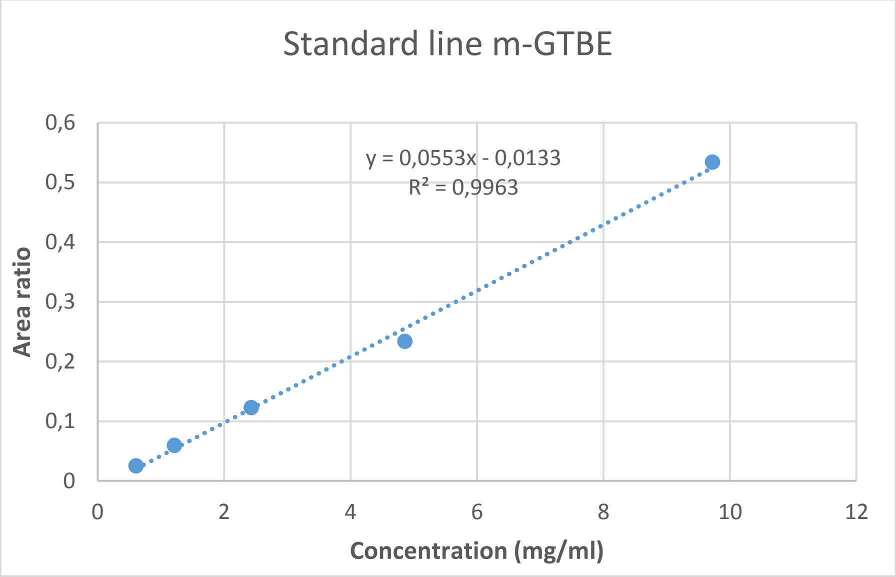

Figure 42: Standard line for m-GTBE

From this standard line, the concentration of m-GTBE can be calculated.

These standard lines served multiple purposes. The conversion of glycerol could be calculated with these standard lines too and compared to the other way of calculation that is described earlier. The selectivity for m-GTBE was calculated by means of the m-GTBE standard line. In addition, the quantification was carried out using these standard lines.

4.3 Statistical validation

Before any experimental value can be used to draw conclusions, a statistical validation has to be carried out to ensure representative values and correct measurements.

The reproducibility was tested by use of the three center points. The calculated standard deviation for the selectivity and conversion is displayed in Table 12.

Table 12: Standard deviation of selectivity and conversion for three center points

Selectivity at center point 1 (%)	51.5
Selectivity at center point 2 (%)	51.9
Selectivity at center point 3 (%)	52.5
Standard deviation	0.5
Conversion at center point 1 (%)	40.3
Conversion at center point 2 (%)	41.3
Conversion at center point 3 (%)	41.9
Standard deviation	0.8

The selectivity in the center point is given as: 52.0 ± 0.5. The conversion in the center point can be expressed as 41.1 ± 0.8. However, it should be noted that for a correct determination of the standard deviation, 8 or more measuring points should be used. The standard deviation on the yield can be determined as follows in Table 13:

Table 13: Determination standard deviation of yield

	Minimal	Maximal	Mean	Standard deviation
Selectivity	40,3	42,0	41,15	0,82
Conversion	51,4	52,5	51,97	0,53
Yield	20,7	22,0	21,39	0,64

The yield in the center points can therefore be expressed as 21.4 ± 0.6.

4.4 Quantification of a product

The results for the quantification of the product that was analyzed are displayed in Table 14.

Table 14: Quantification of a product

COMPOSITION OF THE PRODUCT			
Compound	**Mass (g)**	**Moles**	**Weight Percentage (%)**
Glycerol	18.59	0.20	20.06%
Tert. butyl alcohol	50.70	0.68	54.72%
Mono-glycerol tert. butyl ether	6.71	0.04	7.25%
Di- and tri-glycerol tert. butyl ether	7.602-9.20	0.04	8.21-9.93%
Water	6.87-7.44	0.39-0.41	7.42-8.03%
Others	0.00-2.16	/	0.00-2.34%
Total	**92.65 g**		**100%**

As can be seen, the product contained mostly unreacted TBA, although a large amount of TBA had already evaporated when opening the reactor after the reaction (reagents mass: 115.3814 g). By-products, although in small amounts, were detected. It is most likely that more di-ether than tri-ether was formed since earlier literature reported that over Beta Zeolite no tri-ether is formed [5]. The tri-ether is more voluminous and is not formed on Beta Zeolite since its pore size is limited.

When only d-GTBE was formed, the lower limits should be considered. This implies 7.6092 g of d-GTBE, 6.8700 g of water and 2.1644 g of other products. Other products refer to the by-products, formed out of TBA. This could be isobutene, di-isobutene and oligomers.

4.5 Optimization of the etherification of m-GTBE

In

Table 15 the results of the 2^3 experimental design is given. It includes a survey of the calculated conversion and selectivity for every reaction, together with the yield. The calculations for the conversion, selectivity and yield can be found in attachment nr. 4, as well as extra plots to visualize the influence of the specific factors (attachment nr. 5).

Table 15: Results of etherification reactions

Temperature (°C)	Reaction time (h)	Catalyst loading (% of glycerol mass)	Conversion (%)	Selectivity (%)	Yield (%)
80	2	5	20.32	69.68	14.16
80	6	10	35.19	40.65	14.30
95	4	7.5	41.91	51.91	21.76
80	2	10	25.20	75.87	19.12
95	4	7.5	40.28	52.53	21.16
80	6	5	29.71	30.84	9.16
110	2	10	44.97	59.73	26.86
110	6	5	52.94	41.70	22.08
110	2	5	37.32	70.23	26.21
95	4	7.5	41.26	51.48	21.24
110	6	10	63.22	31.52	19.93

No outliers were detected after checking the results by means of a box plot.
To check linearity, the mean from the center points was evaluated against the mean of the design points for each response. As an example this will be done for the optimization for the selectivity (4.5.1). For conversion and yield the check for outliers and linearity can be found in attachment nr. 6.

The optimization was carried out to determine the optimal conditions for a maximal yield of m-GTBE.
Firstly the response function for the conversion and selectivity is established, followed by the design of a response function for the yield.

4.5.1 Optimization of the selectivity for m-GTBE

Linearity check

Since only two levels were tested, only a linear model can be applied to predict the yield for different values. However, it is not sure whether or not a linear model suffices.

Before checking the linearity, a check for outliers is necessary. The critical values to determine the lower and upper limit are displayed in Table 16.

Table 16: Determination of lower and upper limit for outliers

Minimum	30.8
First quartile	41.2
Median	51.9
Third quartile	64.7
Maximum	75.9

$$IQR = first\ quartile - third\ quartile = 23.5$$
$$Lower\ limit = first\ quartile - 1{,}5 \cdot IQR = 6.0$$
$$Upper\ limit = third\ quartile + 1{,}5 \cdot IQR = 100.0$$

When comparing the results of selectivity with the upper and lower limit, no values are found outside this range. Therefore, it can be concluded that no outliers are present.

The next step is to check the linearity. This can be done by comparing the mean of the center points to the mean of the design points, by means of a t-test. Because the use of a t-test requires input about variance (same or different), an F-test is carried out first to check if the variation of design and center points are equal.

Table 17**Fout! Verwijzingsbron niet gevonden.** includes the output of the f-test that was carried out on the data of yield.

Table 17: F-test for selectivity for m-GTBE

	Design points	*Center points*
Mean	52.52	51.97
Variance	339.18	0.28
Observations	8	3
Degrees of Freedom	7	2
F	1212.39	
P(F<=f) one sided	**0.00082**	
Critical area of F-test : one sided	19.35	

The zero hypothesis of an F-test is that two variables have equal variances. The p-value is lower than 0,05, which implies that, with 95% confidence, these two variables have unequal variances. This means that a t-test for populations with unequal variances has to be carried out.
The output of this t-test is shown in Table 18**Fout! Verwijzingsbron niet gevonden.**.

Table 18: t-test for unequal variances for yield of m-GTBE

	Design points	*Center points*
Mean	52.53	51.97
Variance	339.19	0.28
Observations	8	3
Estimated difference between to means	0	
Degrees of Freedom	7	
T- statistical data	0.085	
P(T<=t) one sided	0.47	
Critical area of T-test: one sided	1.89	
P(T<=t) two sided	**0.93**	
Critical area of T-test: two sided	2.36	

From this t-test, it can be seen that the p-value higher is than 0,05. It can be concluded that the zero hypothesis, which stated that both populations have equal means, is accepted.

From these tests, it is clear that the means of the design points are equal to the means of the center points. The conclusion is that a linear model and linear equations can be applied.

It is important to note that this linearity is only valid for the tested range. If the temperature is increased, another model is expected since the conversion and selectivity will probably level off.

Significance

The results given in Table 14 were analyzed by Design Expert®.

In a good equation, only the significant factors are included. The significance of the factors can be determined by means of a half-normal probability plot. Other options like a Pareto plot or a normal probability plot were also available.

The half-normal probability plot was used to determine the significant factors, followed by a confirmation by means of a sum of squares analysis (Figure 43, Table 1Table 19).

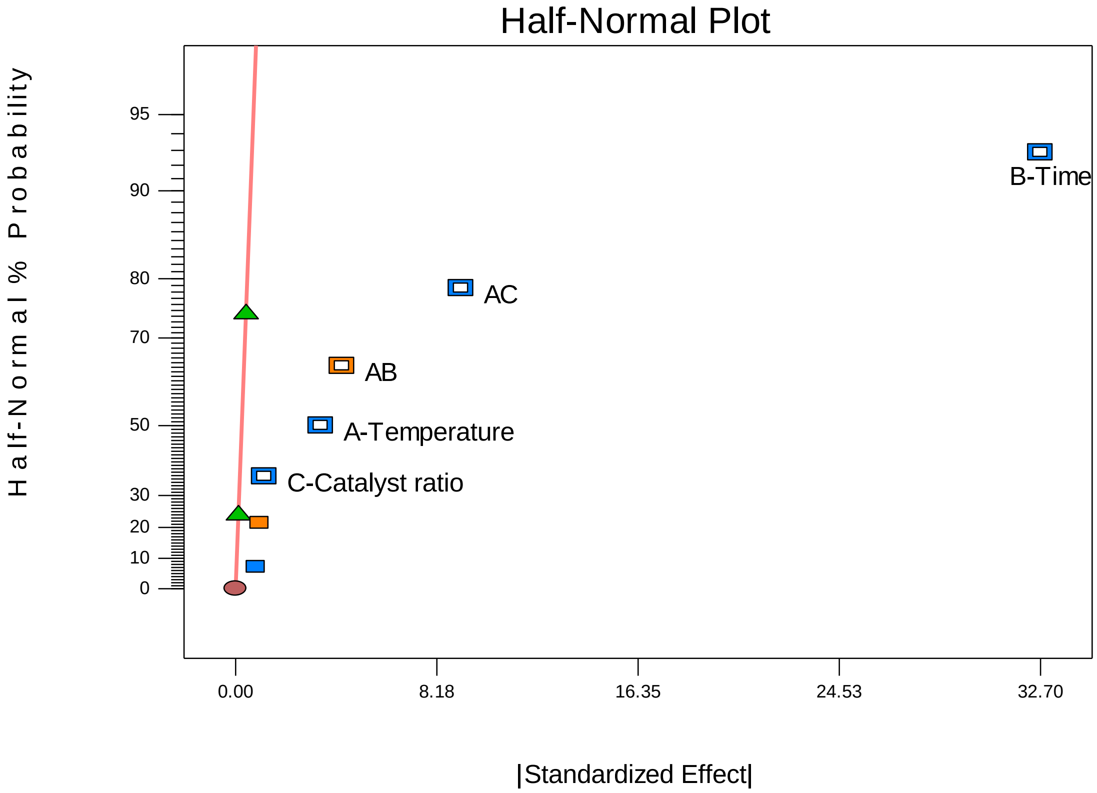

Figure 43: Half-Normal probability plot for determination of the significant factors (Selectivity)

From these results, it can be seen that temperature, time and the interaction between temperature and catalyst loading and temperature and time are the only significant factors. Due to hierarchy, catalyst loading is considered in the equation too. The significance of these factors is confirmed by means of a sum of squares analysis, which is shown in Table 19.

Table 19: Sum of Squares method for optimization of selectivity for m-GTBE

Analysis of variance table [Partial sum of squares - Type III]						
	Sum of		**Mean**	**F**	**p-value**	
Source	**Squares**	**df**	**Square**	**Value**	**Prob > F**	
Model	2371.01	5	474.20	523.52	< 0.0001	significant
A-A	*24.01*	*1*	*24.01*	*26.51*	*0.0036*	
B-B	*2138.58*	*1*	*2138.58*	*2360.98*	*< 0.0001*	
C-C	*2.74*	*1*	*2.74*	*3.02*	*0.1426*	
AB	*37.50*	*1*	*37.50*	*41.40*	*0.0013*	
AC	*168.18*	*1*	*168.18*	*185.67*	*< 0.0001*	
Residual	4.53	5	0.91			
Lack of Fit	*3.97*	*3*	*1.32*	*4.75*	*0.1788*	*not significant*
Pure Error	*0.56*	*2*	*0.28*			
Cor Total	2375.53	10				

Table 20**Fout! Verwijzingsbron niet gevonden.** includes some statistic values about the model of selectivity.

Table 20: Statistics for model of Selectivity for m-GTBE

Std. Dev.	0.95		R-Squared	0.9981
Mean	52.38		Adj R-Squared	0.9962
C.V. %	1.82		Pred R-Squared	0.9813
PRESS	44.44		Adeq Precision	64.497

The following equation (coded values only) can be used to predict the selectivity for m-GTBE:

$$\begin{aligned} Selectivity = 52.38 - 1.73 \cdot Temperature - 16.35 \cdot Time - 0.59 \cdot Catalyst\ loading \\ - 4.59 \cdot Temperature \cdot Catalyst\ loading + 2.16 \ \cdot Temperature \cdot Time \end{aligned}$$

This equation can be used to identify the relative impact by comparing the factor coefficients. It shows the negative effect of temperature, time and catalyst loading on the selectivity. In addition, the interaction between temperature and catalyst loading has a significant negative effect too, while the interaction between temperature and time has a positive influence. Comparing the factors shows the main influence of time on selectivity. This is evident because of the consecutive pathway.

Temperature can have a dual effect on selectivity. An increase in temperature leads to a decrease in viscosity. This eases the mass transfer. The desorption of mono-ether is preferred and the selectivity for m-GTBE increases, this is the first effect. However, the transfer of carbocation to the adsorbed m-GTBE is also facilitated, resulting in a drop in selectivity. This is the second effect.
When the catalyst ratio is low, the first effect is more important and the desorption of m-GTBE is promoted at higher temperatures. Thus, increasing the temperature leads to an increase in selectivity.
At high catalyst ratios, the second effect is more important: since a lot more carbocations are present than at low catalyst ratio, the chances are more likely for m-GTBE to react to d-GTBE, resulting in a decrease of selectivity.

Since the etherification follows a consecutive pathway, the selectivity decreases with time, as mentioned before.

The selectivity for m-GTBE declines with a higher catalyst loading for multiple reasons. Firstly, the chance that adsorbed m-GTBE on the catalyst reacts further to d-GTBE increases because simply more adsorbed m-GTBE is present.
Secondly, an increase in catalyst loading means an increase in acid concentration, which leads to an augmentation in carbocation concentration. This induces a shift of the reaction equilibrium to the right and causes an increase in selectivity towards d-GTBE.

The conditions for the optimal selectivity were determined to be:

- a reaction temperature of 80 °C,
- a reaction time of 2 hours,
- a catalyst loading (% of glycerol mass) of 10 %.

This can be explained as follows:

Temperature has a negative influence on selectivity, as well as reaction time and catalyst loading. Temperature is chosen at its low level of 80 °C, due to its negative influence. Reaction time is also included in the equation twice and should be kept at low level to maximize the selectivity. For the catalyst loading, the interaction with temperature is more important than catalyst loading itself. Hence, the catalyst loading should be kept at high level, to maintain the low level of the factor interaction with temperature.

4.5.2 Optimization of conversion of glycerol

The half-normal probability plot was used to determine the significant factors and is displayed in Figure 44.

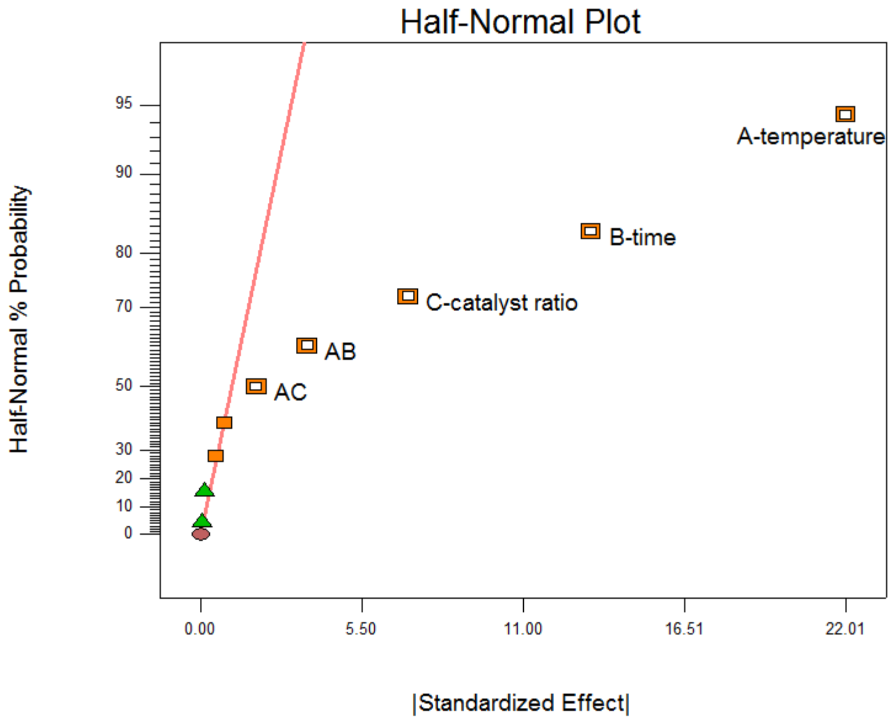

Figure 44: Half-Normal probability plot for determination of the significant factors (Conversion)

From this figure, it is clear that the significant factors are temperature, time, catalyst ratio, the interaction between temperature and time and temperature and catalyst loading. To confirm this, the sum of squares analysis is used, which is shown in Table 21.

Table 21: Sum of Squares analysis for determination of the significant factors (Conversion)

Analysis of variance table [Partial sum of squares - Type III]						
	Sum of		**Mean**	**F**	**p-value**	
Source	**Squares**	**df**	**Square**	**Value**	**Prob > F**	
Model	1456.55	5	291.31	84.41	< 0.0001	significant
A-temperature	*968.66*	*1*	*968.66*	*280.68*	*< 0.0001*	
B-time	*354.45*	*1*	*354.45*	*102.70*	*0.0002*	
C-catalyst ratio	*100.04*	*1*	*100.04*	*28.99*	*0.0030*	
AB	*26.25*	*1*	*26.25*	*7.60*	*0.0399*	
AC	*7.16*	*1*	*7.16*	*2.08*	*0.2092*	
Residual	17.26	5	3.45			
Lack of Fit	*15.91*	*3*	*5.30*	*7.88*	*0.1147*	*not significant*
Pure Error	*1.35*	*2*	*0.67*			
Cor Total	1473.81	10				

Significant values have a p-value lower than 0.05. As can be seen, temperature, time, the catalyst loading and the interaction between temperature and time have a significant effect on the conversion. The lack of fit is not significant, which is desired.

Some important statistical values are displayed in Table 22.

Table 22: Statistics for model of Conversion for m-GTBE

Std. Dev.	1.86		R-Squared	0.9883
Mean	39.30		Adj R-Squared	0.9766
C.V. %	4.73		Pred R-Squared	0.9429
PRESS	84.18		Adeq Precision	30.898

The R² values and precision indicate an adequate signal.

This design results in the following equation:

$$\begin{aligned} Conversion = {} & 39.30 + 11.00 \cdot Temperature + 6.66 \cdot Time + 3.54 \cdot Catalyst\ loading \\ & + 1.81 \cdot Temperature \cdot Time + 0.95\ Temperature \cdot Catalyst\ loading \end{aligned}$$

This equation can only be applied for coded factors.

As can be seen, temperature, time and catalyst loading all have a positive influence on the conversion. The optimal conditions would be:

- a reaction temperature of 110 °C
- a reaction time of 6 h
- a catalyst loading (% of glycerol mass) of 10 %

This result was expected.
It is clear that temperature is the most significant factor. At higher temperatures, the conversion of glycerol increases through the increased reaction rate. However, since the etherification of glycerol is a slightly exothermic reaction, at high temperatures, the reaction gets limited by thermodynamics and the back reaction (de-etherification) could be favored. This is not observed in these experiments thought.

The effect of time is also logical: conversion increases with time since the consecutive pathway is followed.

The conversion of glycerol raises when more catalyst is present. This is logical since more catalyst implies a higher carbocation concentration. Also, more glycerol can be adsorbed on the catalyst that can react to ethers. These two facts result in a higher conversion.

From this optimization, it is clear that the conditions for an optimal conversion do not correspond with the optimal conditions for selectivity (reaction temperature of 80°C, reaction time of 2h and catalyst loading of 10%).

4.5.3 Optimization of yield of m-GTBE

To determine the significance of the factors, again a half-normal probability plot was used. The half-normal probability plot is displayed in Figure 45.

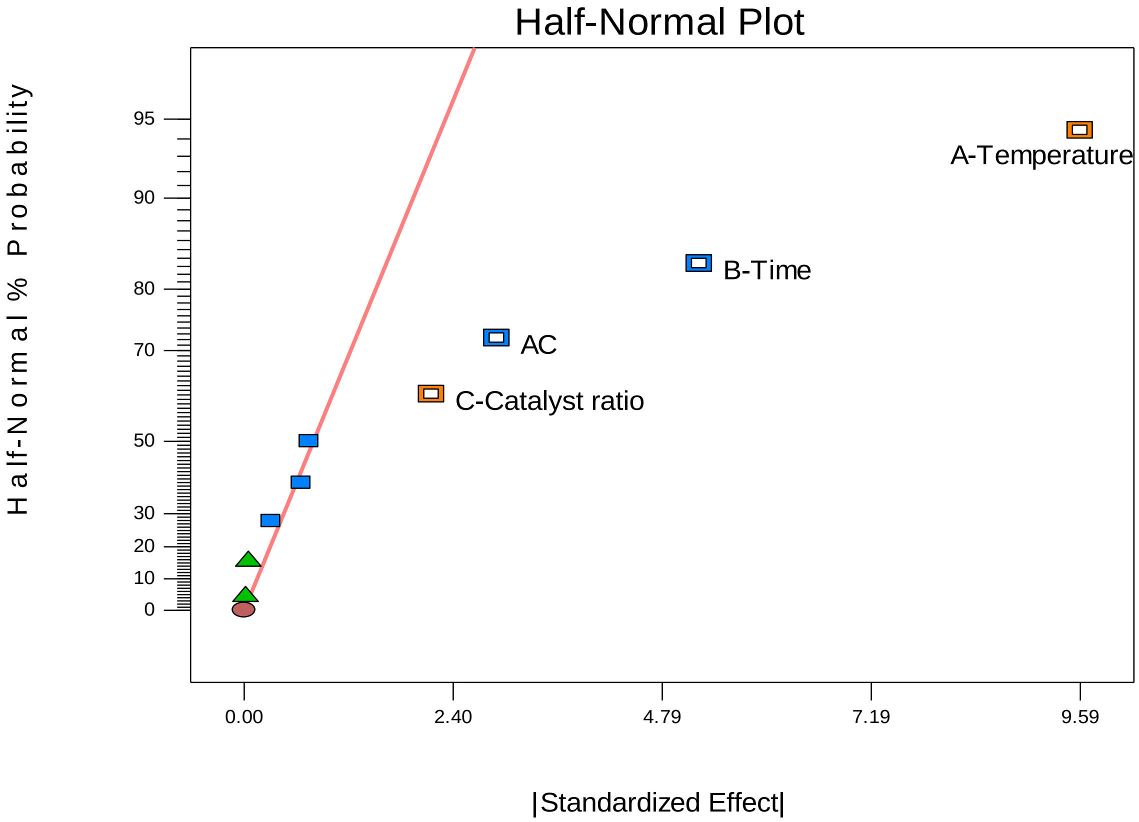

Figure 45: Half-Normal probability plot for determination of the significant factors (yield)

From this figure, it is clear that temperature, time, catalyst loading and the interaction between temperature and catalyst loading possibly are the significant factors. To confirm this, the sum of squares analysis is used, which is shown in Table 23.

Table 23: Sum of Squares analysis for determination of the significant factors

Analysis of variance table [Partial sum of squares - Type III]						
	Sum of		**Mean**	**F**	**p-value**	
Source	**Squares**	**df**	**Square**	**Value**	**Prob > F**	
Model	264.31	4	66.08	26.37	0.0006	significant
A-Temperature	*183.74*	*1*	*183.74*	*73.32*	*0.0001*	
B-Time	*54.50*	*1*	*54.50*	*21.75*	*0.0035*	
C-Catalyst ratio	*9.24*	*1*	*9.24*	*3.69*	*0.1032*	
AC	*16.82*	*1*	*16.82*	*6.71*	*0.0412*	
Residual	15.04	6	2.51			
Lack of Fit	*14.82*	*4*	*3.71*	*34.92*	*0.0280*	*significant*
Pure Error	*0.21*	*2*	*0.11*			
Cor Total	279.34	10				

Significant values have a p-value lower than 0.05. As can be seen, temperature, time and the interaction between temperature and catalyst loading have a significant effect on the yield. Because of hierarchy, the catalyst loading is also considered in the equation.

Some important statistical values are displayed in Table 24.

Table 24: Statistics for model of Yield for m-GTBE

Std. Dev.	1.58		R-Squared	0.9462
Mean	19.63		Adj R-Squared	0.9103
C.V. %	8.06		Pred R-Squared	0.8391
PRESS	44.95		Adeq Precision	16.589

The R² values and precision indicate an adequate signal. From the sum of squares analysis the lack of fit appears to be significant, which is undesired.
It would be better to extend the experiments with extra points to check for curvature and quadratic significance.

This analysis results in the following equation:

$$Yield = 19.63 + 4.79 \cdot Temperature - 2.61 \cdot Time + 1.08 \cdot Catalyst\ loading - 1.45 \cdot Temperature \cdot Catalyst\ loading$$

This equation can only be applied for coded factors.
The optimal conditions for a maximal yield of m-GTBE were:

- a reaction temperature of 110 °C,
- a reaction time of 2 h,
- a catalyst loading (% of glycerol mass) of 5 %.

The effects are explained in the next paragraph. Despite the positive effect of catalyst loading on the yield, a low catalyst loading combined with high reaction temperature results in maximal yield, because the interactions' influence is more important than the influence of the catalyst loading.

Graphics and plots of effects and residues

The significant effects can be plotted to inspect their influence on the yield of m-GTBE.

First, the main effects are displayed in Figure 46.

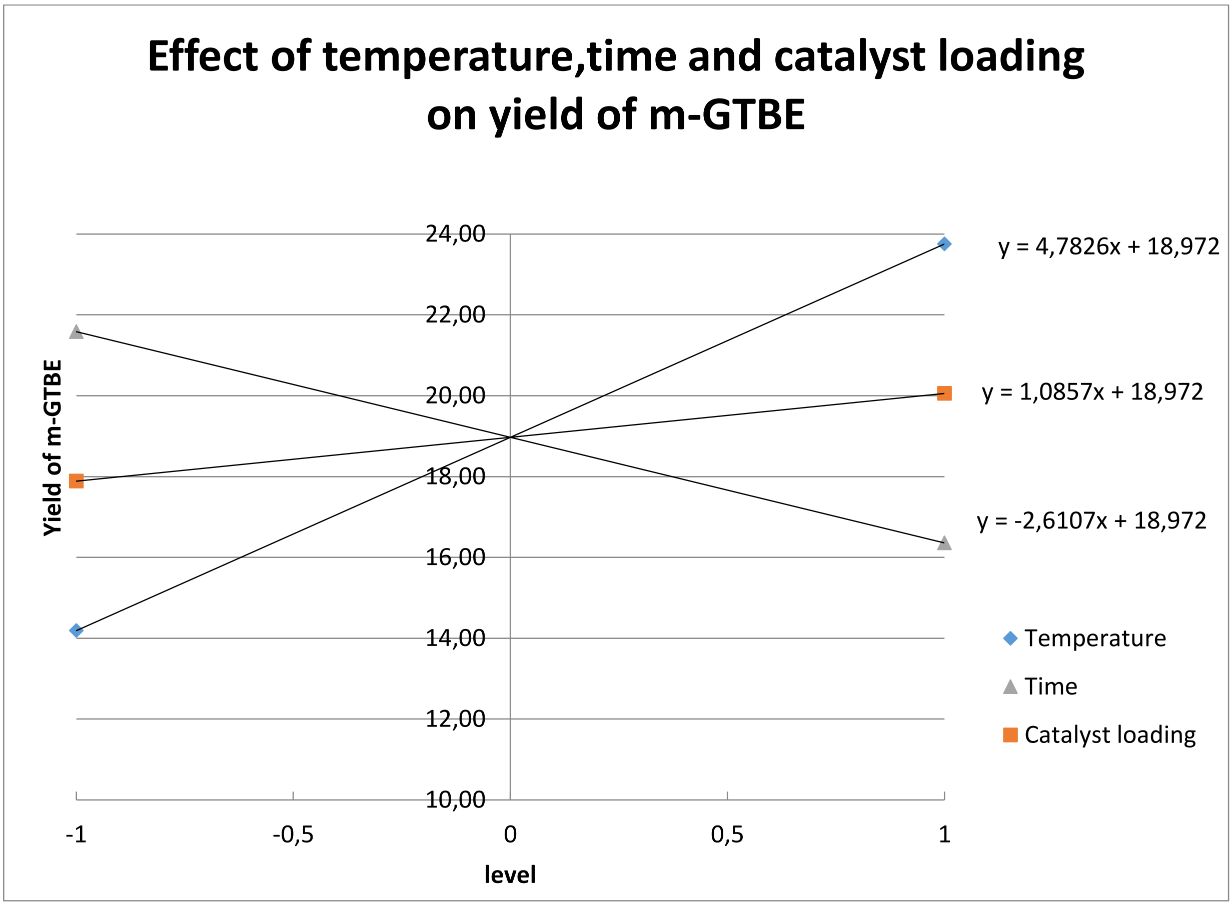

Figure 46: Main effects on the yield of m-GTBE

Temperature

It is clear that temperature is the most significant factor, having an overall positive effect on the yield of m-GTBE (besides the factor-factor interactions). The combination of both selectivity and conversion leads to the yield. The increase in conversion is more significant than the decrease/increase in selectivity, leading to a general increase in yield with the reaction temperature. Later in this thesis, these results are compared with the optimization of the etherification of glycerol with Amberlyst 36 Wet.

Time

Time has a negative effect on the yield. The conversion increases with time. The selectivity for m-GTBE decreases since the etherification follows a consecutive pathway. The combination of these two effects leads to a global decrease, since the decrease of selectivity is more significant than the increase of conversion.

Catalyst loading

Catalyst loading has globally a slightly positive effect on the yield.
To maximize the selectivity and the conversion, a high catalyst loading should be used. However, a maximal yield is reached at low catalyst loading, because the interaction term (temperature-catalyst loading) is more important than the term of catalyst loading itself.

Temperature-catalyst loading interaction

The temperature-catalyst loading interaction is shown in Figure 47.

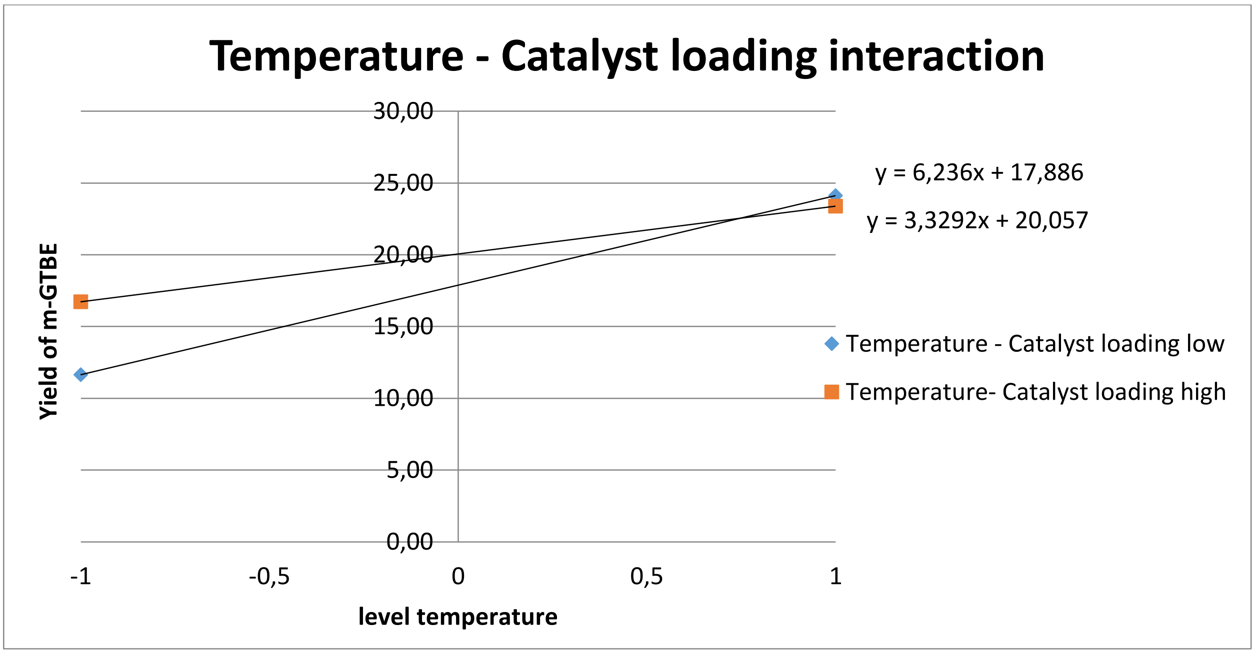

Figure 47: Temperature-catalyst loading interaction

From Figure 47 it is clear that temperature and catalyst loading interact with each other. At high catalyst loading, the positive effect of temperature on the yield is less than with low catalyst loading. At high temperature the effect of the catalyst loading on the yield is minimal (in the plot, both points are almost equal).

Design Expert® can be used to draw 3D-plots for the calculated model. In Figure 48 a 3D plot is given with the catalyst loading set on 5% (low level).

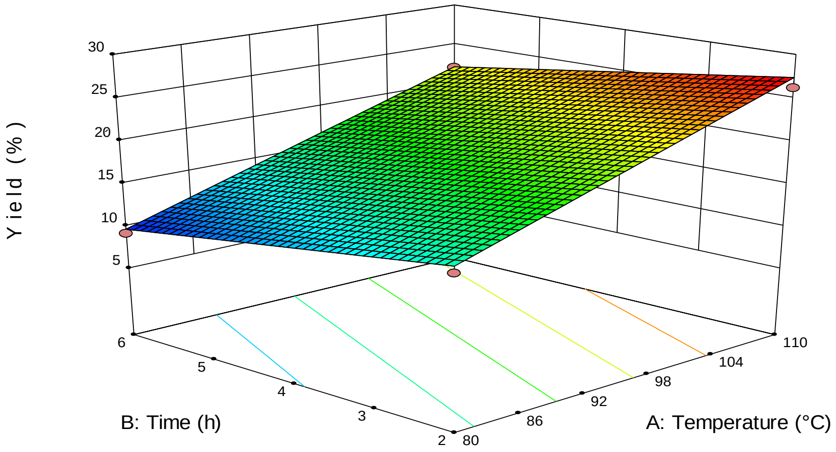

Figure 48: 3D-plot for influence of temperature and time on yield of m-GTBE (catalyst was set at low level)

To optimize the reaction, the temperature should be kept at high level while catalyst loading and time should be kept at low level, according to this model. The upper temperature of 110 °C could be exceeded but at 120 °C, side reactions limit the conversion so one has to remain cautious when varying the temperature.

In Figure 49, the predicted values are visualized in a cube. This cube can be used to compare the yield of m-GTBE at high and low catalyst ratio.

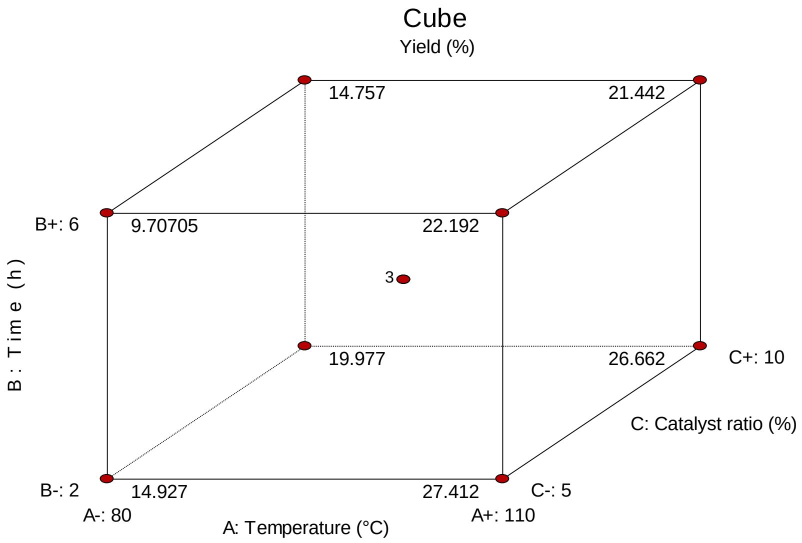

Figure 49: Design cube for model of Yield of m-GTBE

From this figure, it can be seen that working at low catalyst loading leads to a yield of 27.4 %, while working at high catalyst loading results in a yield of 26.7 %. Since the standard deviation on the yield is 0.6, this is only a very small improvement. This leads to the conclusion that the amount of catalyst can be chosen high (improves the conversion) or low (improves the selectivity at high temperatures), both options will result in approximately the same yield.

4.6 Comparison with the etherification using Amberlyst 36 Wet

For this thesis, the etherification of glycerol was carried out by using Beta Zeolite as catalyst. Another possibility is the use of Amberlyst 36Wet, which was tested and optimized by another student. The results of both catalysts are compared and discussed in this section.

However, it has to be noted that the optimization with Beta Zeolite is a full factorial experiment, while the optimization with Amberlyst was established by varying one factor at a time, not including the factor interactions. This explains the different ways of presenting the results.

4.6.1 Effect of the temperature

The influence of the reaction temperature on the conversion and selectivity in the reaction with Amberlyst is shown in Figure 50.

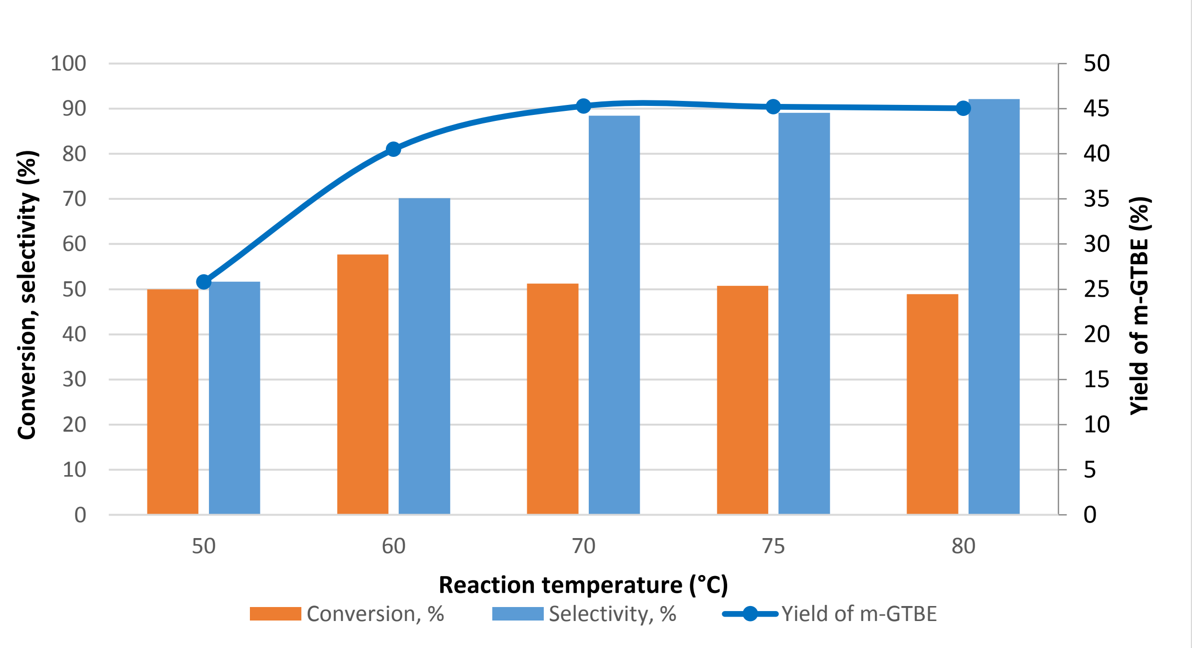

Figure 50: Influence of reaction temperature on etherification with Amberlyst 36Wet (TBA/Gly: 4/1; 6h; 7.5 % catalyst; 10 atm)

As can be seen, the reaction temperature is significantly lower than the reaction temperature with Beta Zeolite. This depends on the activation temperature of the catalyst: the activation temperature of Amberlyst 36Wet is lower than the activation temperature of Beta Zeolite.

Some more differences can be remarked: firstly, the conversion does only increase slightly when the temperature increases to 60°C and drops afterwards. The selectivity towards m-GTBE increases up to 92 % which is much higher than the selectivity with Beta Zeolite. The overall effect remains the same: an increase of the yield of m-GTBE with increasing temperature. Amberlyst 36Wet is more acid than Beta Zeolite (5,4 mmol/g compared to 1,03 mmol/g [5]). This could explain the higher conversion. The higher selectivity however, is unexpected since the pore size of Amberlyst 36Wet is much bigger (24 nm compared to 0.55 nm). The smaller pore size of Beta Zeolite should result in a higher selectivity for m-GTBE. More research should be carried out to investigate this phenomenon.
The combination of a higher selectivity and higher conversion results in a significantly higher yield of m-GTBE: for Beta Zeolite, the maximal yield that was reached was 26. 9 %.

4.6.2 Effect of the reaction time

The influence of the reaction time on the conversion and selectivity with Amberlyst 36Wet is shown in Figure 51.

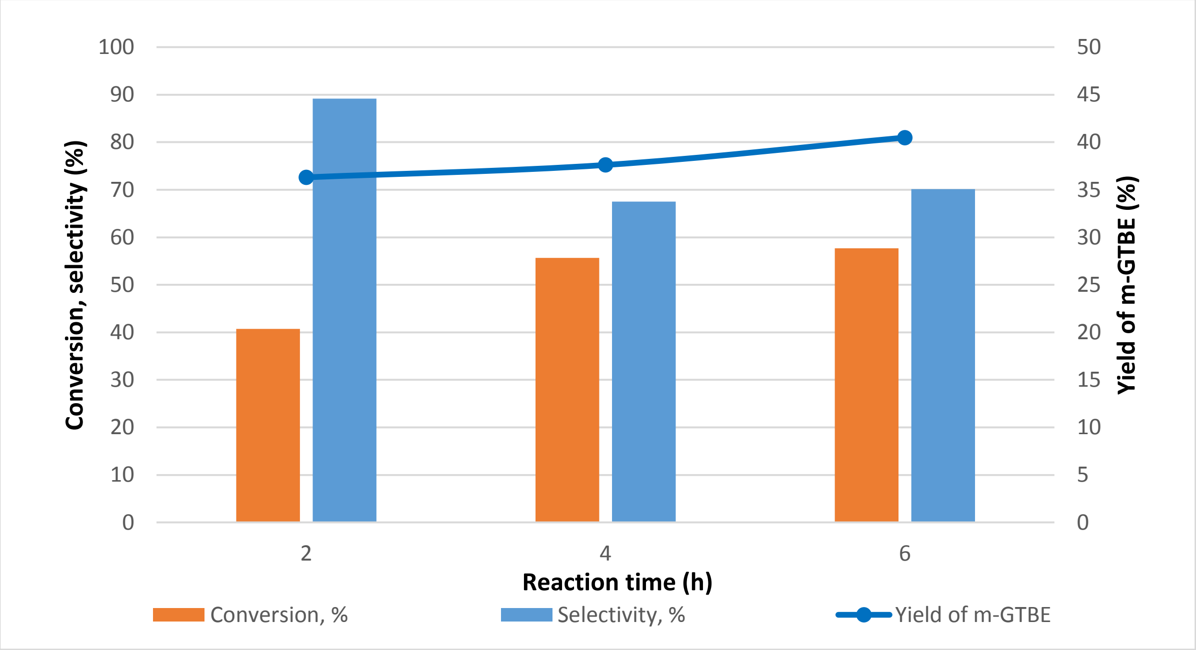

Figure 51: Influence of reaction time on etherification with Amberlyst 36Wet (TBA/Gly: 4/1; 70 °C; 7.5% catalyst; 10atm)

The effect of reaction time on conversion and selectivity is the same as with the use of Beta Zeolite: the conversion increases and the selectivity decreases. The selectivity decreases since m-GTBE is the first product in a consecutive reaction path way and reacts further to d-GTBE.

4.6.3 Effect of the catalyst loading

The influence of the catalyst loading on the conversion and selectivity is shown in Figure 52.

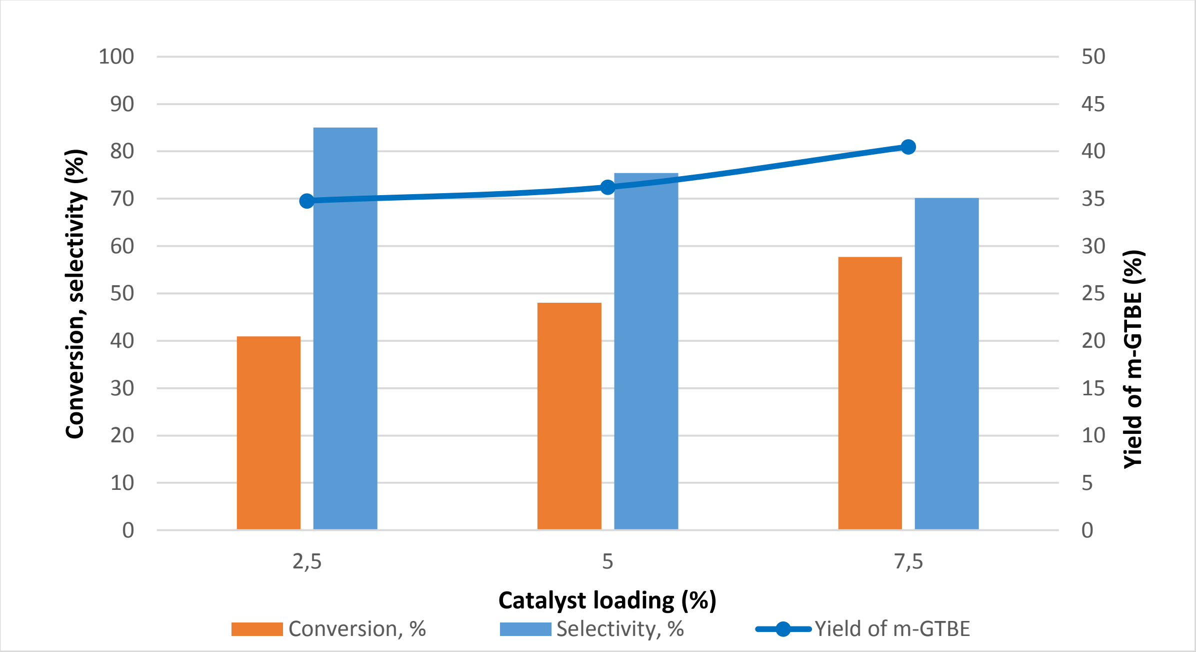

Figure 52: Influence of catalyst loading on etherification with Amberlyst 36Wet (TBA/Gly:4/1; 6h; 70 °C; 10atm)

The influence of catalyst loading on the conversion of glycerol is similar to the reaction with Beta Zeolite. The selectivity decreases with increasing catalyst loading, which can be explained by several reasons, as mentioned before, such as the increased acidity and the statistical chance of reacting further.

The maximal yield with Beta Zeolite was 110°C, 2h and a catalyst loading of 10 wt%. The corresponding yield was 26.86 %. When using Amberlyst 36Wet, the maximal obtained yield was 49.93 %. This was obtained after 6h of reaction, with 7.5 % catalyst and at 70°C. A higher molar ratio TBA/Gly was used (6/1 instead of 4/1) and the catalyst was dried at 90°C in vacuum before using it.

The optimization with Amberlyst 36Wet was carried out according to a one-factor-at-a-time technique. Since the optimization with Design Expert® revealed the significance of the temperature-catalyst loading interaction, the experiment with Amberlyst 36Wet could be extended with experiments that account for this interaction.

4.7 Separation purity

m-GTBE is isolated from the mixture in two steps with a normal distillation being the first step, followed by a vacuum distillation.

In this section, one example of normal distillation is shown, followed by a table that includes the separation efficiency for all normal distillations. The results for the first distillation are displayed in Table 25.

Table 25: Results for normal distillation 1

BEFORE		**AFTER**	
Peak ratio		Peak ratio	
0.83		0.17	
Conc. TBA	vial	Conc. TBA	vial
31.56	mg/ml	4.91	mg/ml
Conc. TBA	mixture	Conc. TBA	mixture
789.10	mg/ml	122.79	mg/ml
Total TBA	mixture	Total TBA	mixture
120.42	g	5.96	g
SEPARATION EFFICIENCY			**95.05%**

A separation of 95.05 % means there was still 5.96 g of TBA present in the mixture when started with an amount of 120.4233 g TBA. This was no problem since in the vacuum distillation, water and TBA would form the first fraction and were still separated from the mixture.

8 normal distillations were carried out of which the efficiencies are displayed in Table 26.

Table 26: Normal distillation efficiencies

Distillation	Separation efficiency (%)
1	95
2	95
3	98
4	94
5	98
6	97
7	92
8	95

It can be seen that the average separation efficiency was 96 ± 2 %. This is sufficient since TBA and water were also collected in the vacuum distillation.

In the next step, all distillates were collected and subjected to a vacuum distillation.
The composition of the distillate after vacuum distillation is calculated and shown in Table 27.

Table 27: Results for vacuum distillation 1

BEFORE		**AFTER**	
Peak ratio		Peak ratio	
0.72		1.10	
Conc. m-GTBE	vial	Conc. m-GTBE	vial
14.81	mg/ml	22.54	mg/ml
Conc. m-GTBE	mixture	Conc. m-GTBE	mixture
370.26	mg/ml	563.60	mg/ml
Total TBA	mixture	Total TBA	mixture
53.59	g	33.00	g
SEPARATION EFFICIENCY			**61.57%**

This table illustrates the difficulty in distilling m-GTBE: it is very hard to distill without losing m-GTBE to the receiving flask together with the earlier fractions of TBA, water and d- and t-GTBE. The reason for this is the local overheating. When a capillary is used to prevent this, the efficiency rises (see Table 28**Fout! Verwijzingsbron niet gevonden.**). Another difficulty was the fact that glycerol is undesired in the receiving flask because it is undesired in the m-GTBE product. It seemed very hard to distill m-GTBE without also distilling glycerol, so small losses of m-GTBE were inevitable.

In Table 28, the results for a vacuum distillation with capillary are shown.

Table 28: Results for vacuum distillation with capillary

BEFORE		**AFTER**	
Peak ratio		Peak ratio	
0.18		0.97	
Conc. m-GTBE	sample	Conc. m-GTBE	sample
3.71	mg/ml	20.03	mg/ml
Conc. m-GTBE	mixture	Conc. m-GTBE	mixture
92.74	mg/ml	500.87	mg/ml
Total m-GTBE	mixture	Total m-GTBE	mixture
12.23	g	12.19	g
SEPARATION EFFICIENCY			**99.69%**

It is clear that the capillary improves the separation efficiency significantly. Almost all m-GTBE is distilled. The small loss can be attributed to the difficulty of distilling m-GTBE without also distilling glycerol.

In the vacuum distillation, the first fraction holds TBA and water. The second fraction consists of m-GTBE and small amounts of d-GTBE. The third fractions is glycerol and some m-GTBE. The typical composition of the vacuum distilled product is displayed in Table 29.

Table 29: Typical fractions in vacuum distillation

Vacuum distillation		
m-GTBE	8.57	wt%
TBA + Water	1.93	wt%
Glycerol+m-GTBE	89.50	wt%

As can be seen, the average yield of m-GTBE after a vacuum distillation is only 8.57 wt%. The final amount of m-GTBE is even lower since multiple distillations are necessary to remove all glycerol and d-GTBE.

The average efficiency of vacuum distillation was 79 %.

4.8 Influence of m-GTBE on characteristics of pure gasoline

4.8.1 Oxygen content

The oxygen content was calculated by means of GC-MS. The spectra and calculations are included in attachment 7.
The oxygen content for the different blends is displayed in Table 30

Table 30: influence of m-GTBE on oxygen content of pure gasoline

% m-GTBE added to gasoline	wt% oxygen in gasoline
2.5	1.2
5	1.4
7.5	1.7

It can be seen that the addition of m-GTBE results in a higher oxygencontent. This is logical since m-GTBE is an oxygen rich compound since one molecule contains 3 oxygen atoms.

The oxygen content in gasoline in Europe, America and most parts of Asia is limited to 2.7 wt%. All percentages of m-GTBE that were tested meet this requirement.

4.8.2 Fractionated distillation

The results of the fractionated distillation are displayed in Table 31.

Table 31: Fractionated distillation of different blends of gasoline with m-GTBE

	Temperature (°C)			
	Pure gasoline	**2.50%**	**5%**	**7.50%**
Initial boiling point	40	40	40	40
10%	52	54	52	54
20%	60	64	64	64
30%	68	74	74	76
40%	76	80	82	86
50%	84	92	94	96
60%	96	100	104	110
70%	118	122	122	126
80%	134	138	140	142
90%	154	162	166	170
Final boiling point	164	184	190	192
	Residue (v %)			
	0,3	1,1	1,9	2,8
	Loss (v %)			
	1,2	1,3	1,2	1

These results are integrated in a graph (Figure 53) to easily present the influence of m-GTBE on the boiling points.

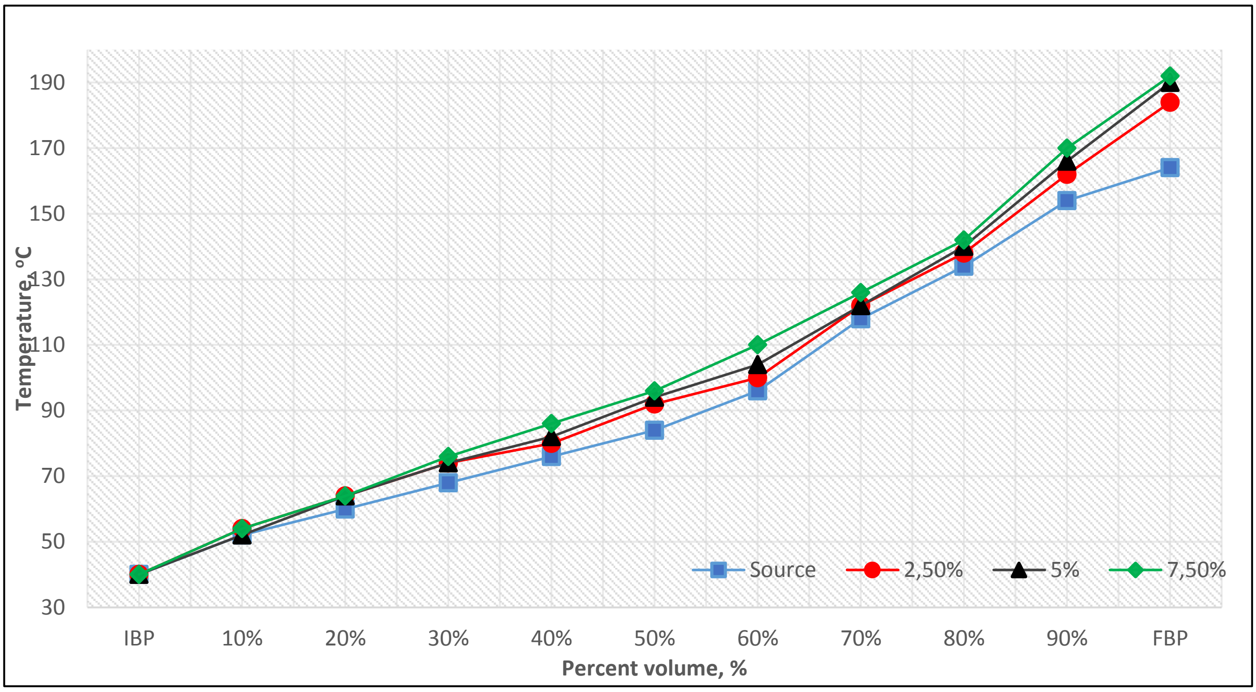

Figure 53: Graph with results of fractionated distillation

From this graph, it is clear that m-GTBE increases the boiling points. As mentioned earlier in Table 7, the boiling points are prescribed by European regulations.

When comparing these results with the regulations, it is clear that the pure gasoline almost reaches the requirements. The only exception is the final boiling point, which is 164 °C and should be at least 170 °C. Therefore, the addition of m-GTBE could be interesting. The addition of m-GTBE in percentages of 2.5, 5 and 7.5 % do not lead to the desired results: the boiling points are too high. A solution could be the addition of m-GTBE in lower percentages than 2.5%. The maximal residue after distillation should not exceed 2 v%. This limit is exceeded for the blend with 7.5 % m-GTBE.

4.8.3 Density

The values for density for different percentages of m-GTBE are displayed in Figure 54.

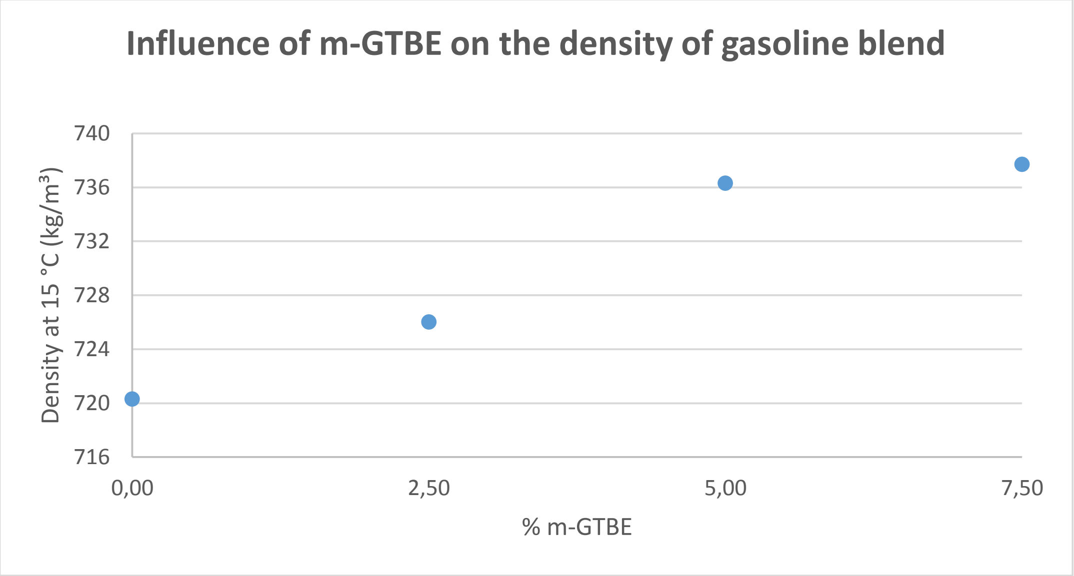

Figure 54: influence of m-GTBE on the density of the gasoline blend

It can be seen that m-GTBE raises the density of the gasoline blend.
This result was expected since the density of gasoline is rather low. m-GTBE is an oxygen rich compound with a low ratio of hydrogen to carbon. This causes an increase in density.

For European regulations (E5), the density at 15°C should be between 743 kg/m^3 and 756 kg/m^3. The density of the pure gasoline does not meet these requirements: it is too low. The addition of m-GTBE to the gasoline can be interesting to help meeting the requirements. However, more than 7.5 wt% should be added.

4.8.4 Vapor pressure

The evolution of the vapor pressure as function of the percentage m-GTBE is displayed in Figure 55.

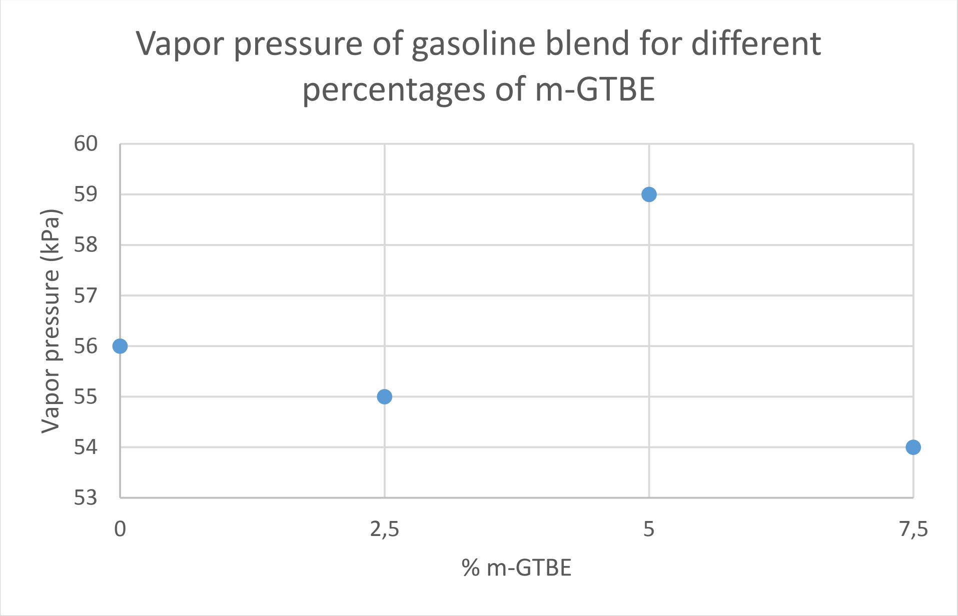

Figure 55: Influence of m-GTBE on the vapor pressure of the blend

The European law prescribes a vapor pressure between 45 kPa and 60 kPa (for the summer period). This requirement is met. The addition of m-GTBE leads to a small decrease in vapor pressure at first but causes an increase at 5.0 %. Afterwards, the vapor pressure decreases again and drops below the original vapor pressure. The minimum vapor pressure is 54 kPa, which is exactly the prescribed minimal vapor pressure.

A high vapor pressure implies a high volatility. This is undesired since it causes high evaporative emissions. To reduce the vapor pressure is one of the most cost-effective ways to reduce the hydrocarbon emissions [53].
In winter however, when low temperatures can cause ignition problems, a higher vapor pressure is needed. Regulations prescribe minimum vapor pressure between 55 and 85 kPa, depending on the country's climate.

For the above reasons, gasoline requires different vapor pressures in winter than in summer. The addition of m-GTBE could offer possibilities in adjusting this vapor pressure. However, more percentages of m-GTBE should be tested to determine the precise impact and limitations of m-GTBE on the gasoline.

5 Conclusions and recommendations

From this research, several conclusions can be made. First, conclusions about the etherification of glycerol are drawn, followed by some recommendations for future research. The second section summarizes the influence of m-GTBE on pure gasoline.

5.1 Etherification of glycerol with tert. butyl alcohol and Beta Zeolite

The etherification of glycerol was carried out with TBA as reagent and Beta Zeolite as catalyst. This research has shown the following facts:

- Temperature has a positive influence on the conversion of glycerol. The influence on selectivity however is ambiguous. The highest yield of m-GTBE was reached at 110°C. Working above this temperature could possibly give higher yield but attention has to be paid at the increased risk for side reactions that drop the conversion;
- Time globally has a negative effect on the yield of m-GTBE: the decrease in selectivity (due to the consecutive pathway) has a larger effect than the increase in conversion;
- The catalyst loading has a positive effect on the conversion. For an optimal selectivity, it is best to keep the catalyst ratio at a high level because of the interaction with temperature. The effect of catalyst loading at high temperature and low time is minimal;
- A linear model was proposed to describe the yield as function of time, temperature and catalyst loading. The following equation was found (coded factors only):

  $$\begin{aligned} Yield = 19.63 + 4.79 \cdot Temperature - 2.61 \cdot Time + 1.08 \cdot Catalyst\ loading \\ - 1.45 \cdot Temperature \cdot Catalyst\ loading \end{aligned}$$

  Since the lack of fit and curvature seem significant, more experiments should be performed to elucidate this behavior. The proposed model also showed that the interaction between temperature and catalyst loading is significant, so future “one factor at a time” experiments should be avoided since interactions are not taken into account.
- The comparison with Amberlyst 36Wet shows that Beta Zeolite has a lower selectivity for m-GTBE, combined with a lower conversion, resulting in a lower yield. Therefore, when the aim is to produce m-GTBE, it would be better to work with Amberlyst 36Wet. However, more research should be done to investigate the costs of the total process since Amberlyst 36Wet demands filtration and results in more difficult distillations;
- The vacuum distillation of m-GTBE is problematic: more research should be done to investigate other possibilities for the separation of m-GTBE from the reaction mixture.

5.2 Influence of m-GTBE on pure gasoline

The influence of m-GTBE on pure gasoline was investigated and the following conclusions can be made:

- The process of blending m-GTBE with gasoline is very simple and inexpensive. However, attention has to be paid to the fact that m-GTBE is hydrophilic and moisture in the air has to be avoided when blending;
- m-GTBE causes the density to increase. This is interesting since it can help refineries to meet the requirements;
- The influence of m-GTBE on the vapor pressure is two-sided: at 5%, the vapor pressure increases, while at 7.5 % the vapor pressure decreases and is lower than the initial vapor pressure. This can be used handy since the requirements for vapor pressure depends on the season (summer or winter);
- The addition of m-GTBE increases the boiling point. However, less than 2.5 % m-GTBE is needed to meet the European requirements.
- An increase of the oxygen content of gasoline can be remarked, when m-GTBE is added. In all tested blends, the oxygen content did not exceed the limit of 2.7 wt%.
- Other characteristics should be tested too before m-GTBE can be applied as oxygenate. Health risks, environmental impact and impact on the motor should be investigated too.

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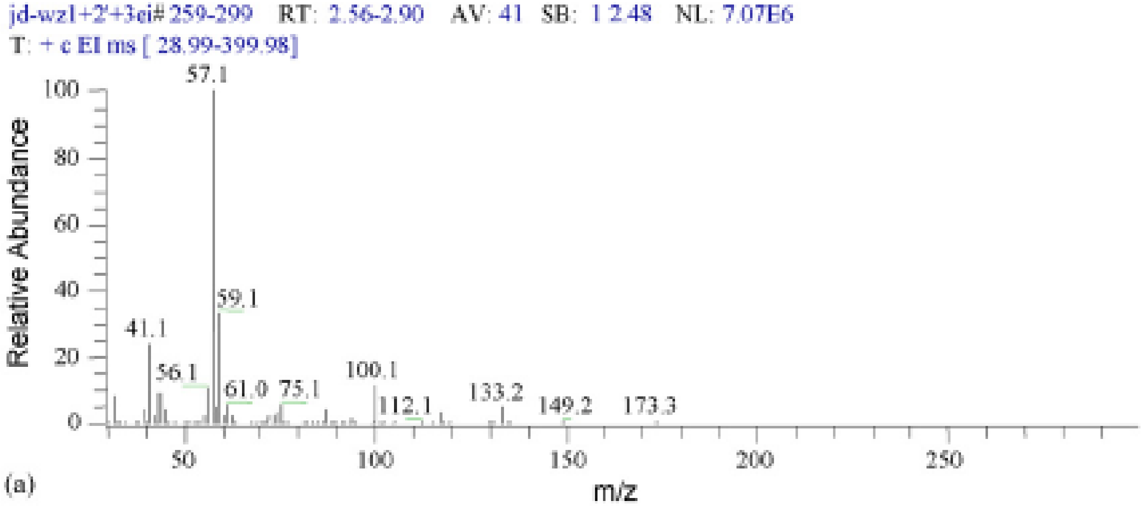
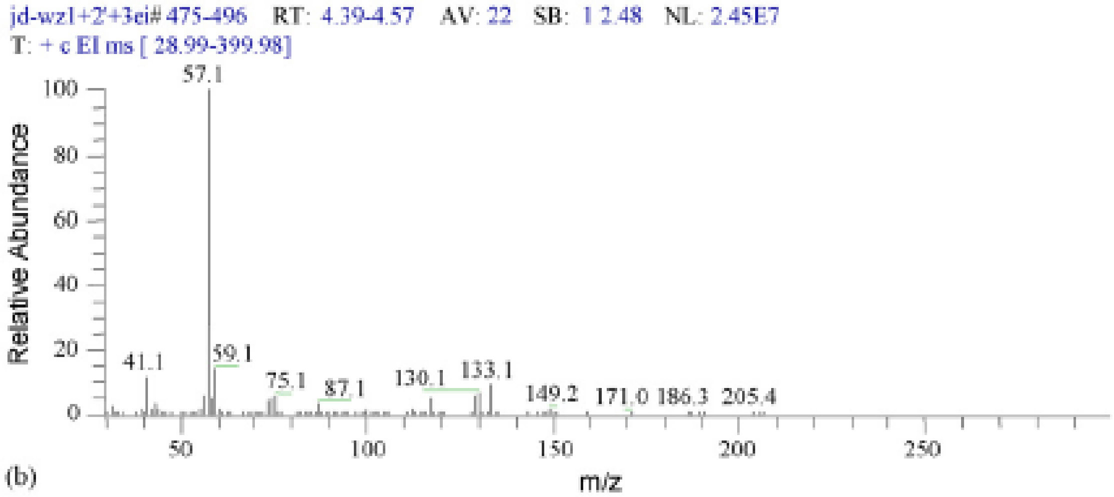
Appendix

Attachment 1: GC-MS spectra for m-, d- and t-GTBE

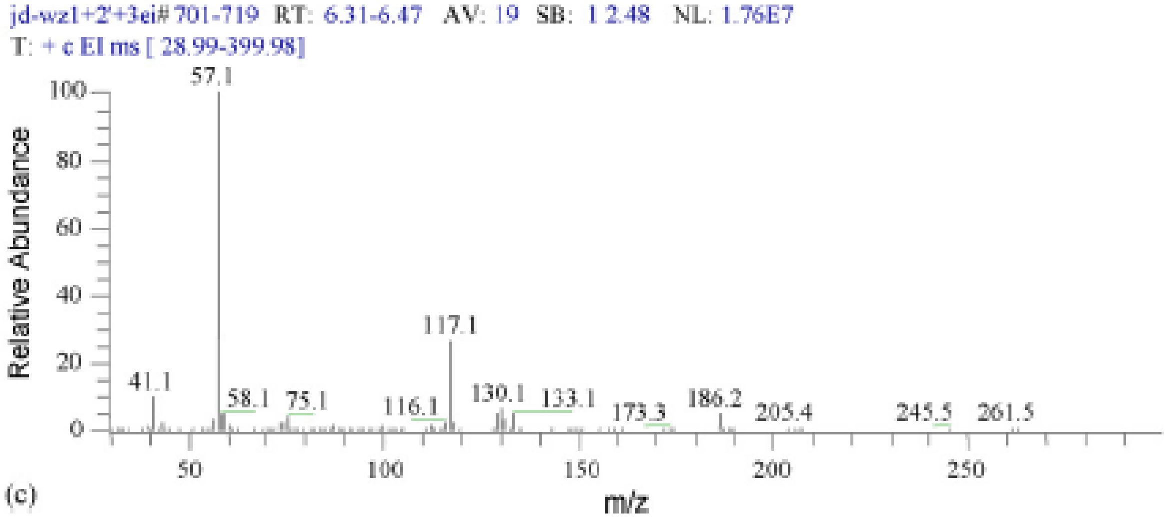
The EI mass spectrum of 3-tert-butoxy-propane-1,2-diol (m-GTBE) [19]**:**



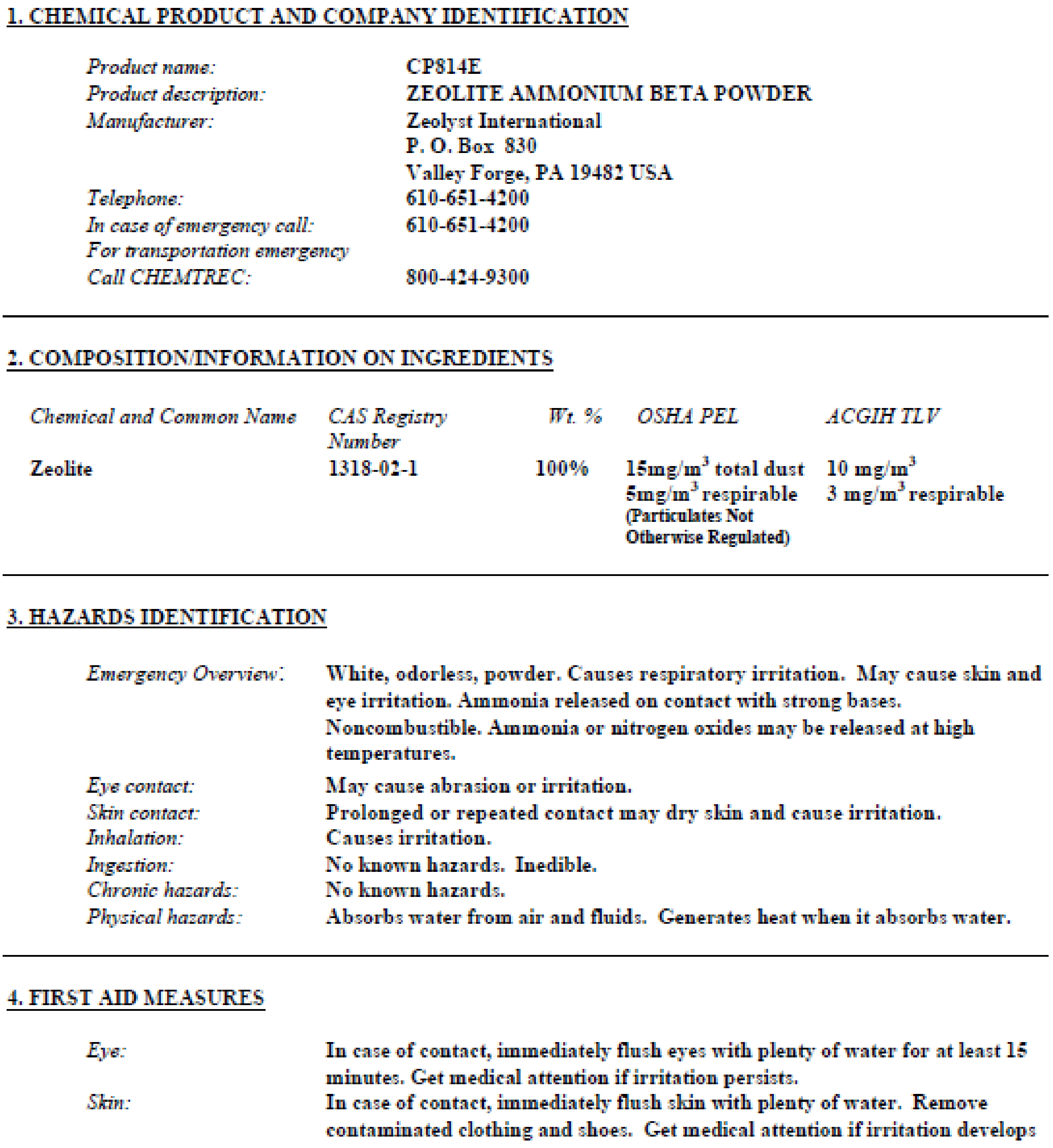
The EI mass spectrum of 1,3-di-tert-butoxy-propane-2-ol (d-GTBE) [19]**:**



The EI mass spectrum of 1,2,3-tri-tert-butoxy-propane (t-GTBE) [19]**:**



Attachment 2: Specifications of Beta Zeolite [54]



1. CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

Product name:	**CP814E**
Product description:	**ZEOLITE AMMONIUM BETA POWDER**
Manufacturer:	**Zeolyst International P. O. Box 830 Valley Forge, PA 19482 USA**
Telephone:	**610-651-4200**
In case of emergency call:	**610-651-4200**
For transportation emergency Call CHEMTREC:	**800-424-9300**

2. COMPOSITION/INFORMATION ON INGREDIENTS

Chemical and Common Name	*CAS Registry Number*	*Wt. %*	*OSHA PEL*	*ACGIH TLV*
Zeolite	**1318-02-1**	**100%**	**15mg/m^3 total dust 5mg/m^3 respirable (Particulates Not Otherwise Regulated)**	**10 mg/m^3 3 mg/m^3 respirable**

3. HAZARDS IDENTIFICATION

Emergency Overview:	**White, odorless, powder. Causes respiratory irritation. May cause skin and eye irritation. Ammonia released on contact with strong bases. Noncombustible. Ammonia or nitrogen oxides may be released at high temperatures.**
Eye contact:	**May cause abrasion or irritation.**
Skin contact:	**Prolonged or repeated contact may dry skin and cause irritation.**
Inhalation:	**Causes irritation.**
Ingestion:	**No known hazards. Inedible.**
Chronic hazards:	**No known hazards.**
Physical hazards:	**Absorbs water from air and fluids. Generates heat when it absorbs water.**

4. FIRST AID MEASURES

Eye:	**In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Get medical attention if irritation persists.**
Skin:	**In case of contact, immediately flush skin with plenty of water. Remove contaminated clothing and shoes. Get medical attention if irritation develops**

	and persists. Wash clothing before reuse. Thoroughly clean shoes before reuse.
Inhalation:	Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.
Ingestion:	Not applicable.

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5. FIRE FIGHTING MEASURES

Flammable limits:	This material is noncombustible.
Extinguishing Media:	This material is compatible with all extinguishing media.
Hazards to fire-fighters:	Ammonia or nitrogen oxides may be released at high temperatures.
Fire-fighting equipment:	The following protective equipment for fire fighters is recommended when this material is present in the area of a fire: self-contained breathing apparatus (SCBA), chemical goggles, body-covering protective clothing, chemical resistant gloves, and rubber boots.

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6. ACCIDENTAL RELEASE MEASURES

Personal protection:	Wear safety goggles, body-covering protective clothing, chemical resistant gloves, and rubber boots, NIOSH-approved dust respirator where dust occurs. See section 8.
Environmental Hazards:	Sinks in water. No know environmental hazards.
Small spill cleanup:	Carefully shovel or sweep up spilled material and place in suitable container. Avoid generating dust. Use appropriate Personal Protective Equipment (PPE). See section 8.
Large spill cleanup:	Keep unnecessary people away; isolate hazard area and deny entry. Do not touch or walk through spilled material. Carefully shovel or sweep up spilled material and place in suitable container. Avoid generating dust. Use appropriate Personal Protective Equipment (PPE). See section 8.
CERCLA RQ:	There is no CERCLA Reportable Quantity for this material. If a spill goes off site, notification of state and local authorities is recommended.

9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance:	White powder.
Odor:	Odorless.
pH:	Not applicable.
Specific Gravity:	>1.
Solubility in water:	Negligible.

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10. STABILITY AND REACTIVITY

Stability:	This material is stable.
Conditions to avoid:	None.
Materials to avoid:	Ammonia may be released on contact with strong bases.
Hazardous decomposition products:	Ammonia, nitrogen oxides.

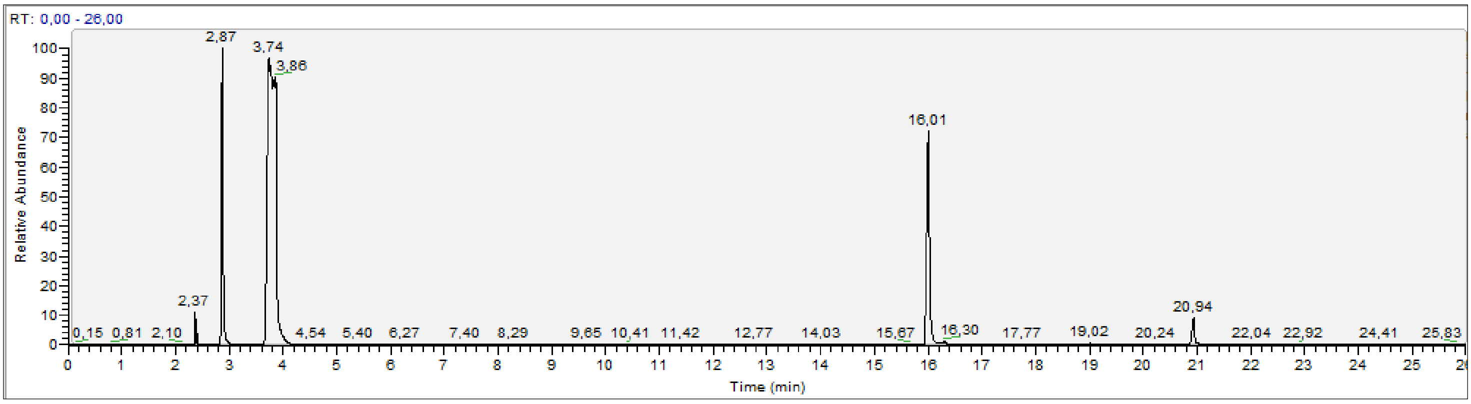
Attachment 3: Typical GC-MS spectra for GTBE-product

Reagent:

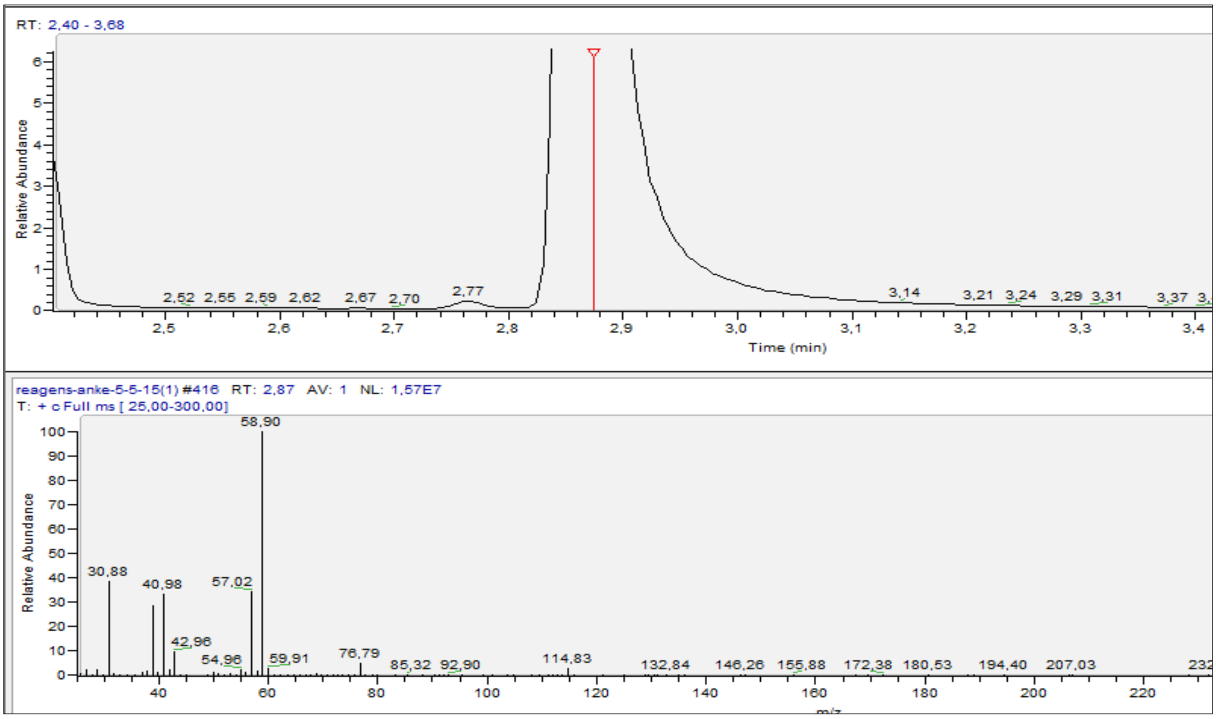
PEAK
LIST
reagens-anke-5-5-15(1).RAW
RT: 2,50 - 3,57
Number of detected peaks: 3

Apex RT	Start RT	End RT	Area	%Area	Height	%Height	Y	
2.87	2,82	2.96	1.03E+08	38.36	52829453	55.18	0.685188	TBA
16.01	15.91	16.36	1.51E+08	55.98	38318809	40.03		Internal Standard
20.94	20.86	21.1	15238621	5.67	4587803	4.79	0.10123	Glycerol

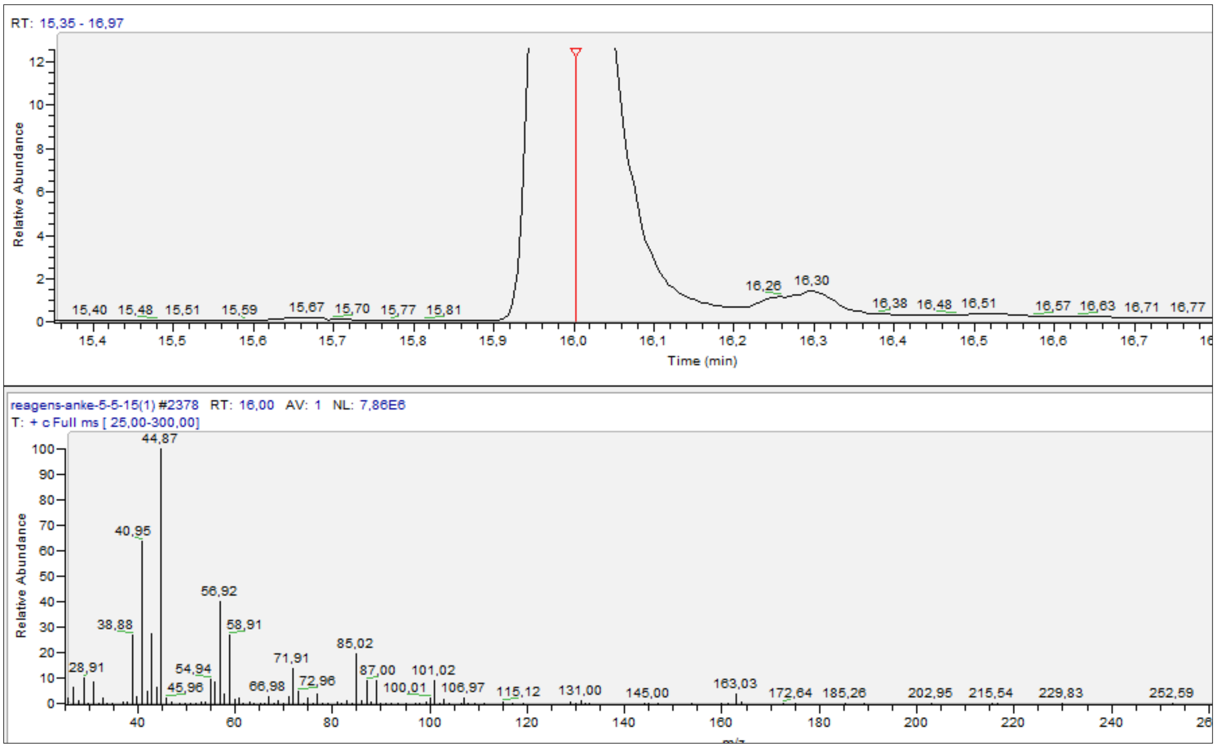
Total GC-spectrum:



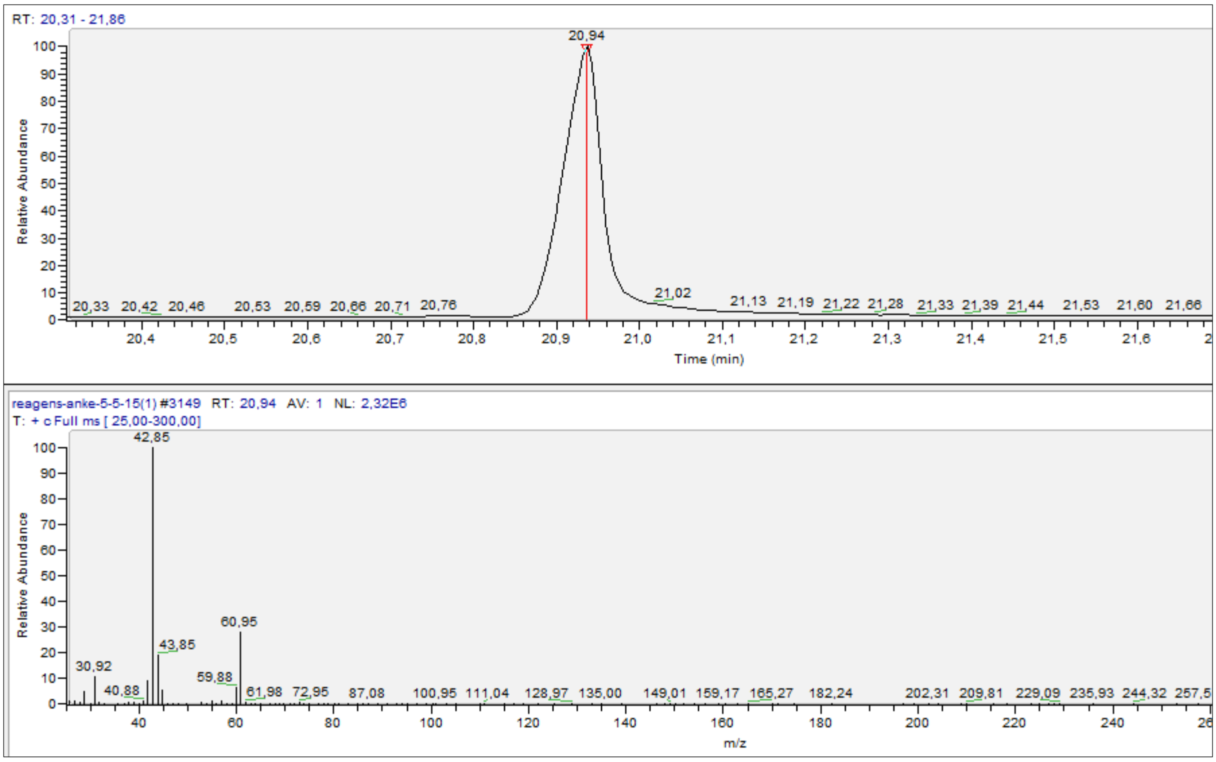
GC-MS-spectrum for TBA:



GC-MS spectrum for internal standard



GC-MS spectrum for glycerol

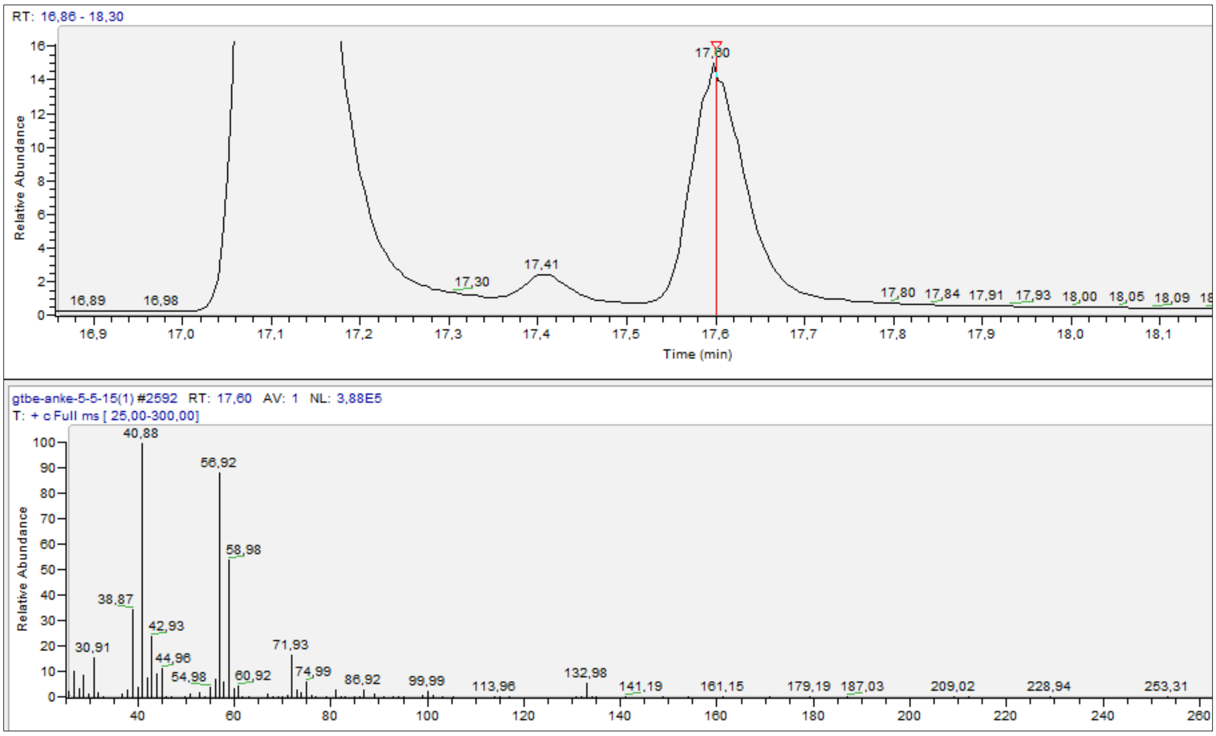


Product:

PEAK
LIST
gtbe-anke-5-5-15(1).RAW
RT: 3.23 - 4.80
Number of detected peaks: 4

Apex RT	Start RT	End RT	Area	%Area	Height	%Height	ratio	
3.97	3.89	4.15	38385674	35.6	11646310	44.5	0.662546	TBA
17.11	17.02	17.49	57936633	53.73	11938858	45.62		Internal Standard
17.6	17.53	17.8	7104392	6.59	1704164	6.51	0.122623	m-GTBE
22.15	22.06	22.31	4412119	4.09	883034.9	3.37	0.076154	Glycerol

GC-MS spectrum for m-GTBE:



Attachment 4: Calculations for the conversion of glycerol

Reaction 1: 80 °C, 6h, 5%

PEAK LIST								
reagens-anke-5-5-15(1).RAW								
RT: 2.50 - 3.57								
Number of detected peaks: 3								
Apex RT	Start RT	End RT	Area	%Area	Height	%Height	Y	
2.87	2.82	2.96	1.03E+08	38.36	52829453	55.18	0.685188	
16.01	15.91	16.36	1.51E+08	55.98	38318809	40.03		Gly/mass
20.94	20.86	21.1	15238621	5.67	4587803	4.79	0.10123	0.1340
PEAK LIST								
gtbe-anke-5-5-15(1).RAW								
RT: 3.23 - 4.80								**Conversion**
Number of detected peaks: 4								29.71%
Apex RT	Start RT	End RT	Area	%Area	Height	%Height	ratio	
3.97	3.89	4.15	38385674	35.6	11646310	44.5	0.662546	
17.11	17.02	17.49	57936633	53.73	11938858	45.62		
17.6	17.53	17.8	7104392	6.59	1704164	6.51	0.122623	Gly/mass
22.15	22.06	22.31	4412119	4.09	883034.9	3.37	0.076154	0.0932

Reaction 2: 95°C, 4h, 7.5%

PEAK LIST								
REAGENS-ANKE-6-4-15(2).RAW								
RT: 2.40 - 3.30								
Number of detected peaks: 3								
Apex RT	Start RT	End RT	Area	%Area	Height	%Height	Y	
2.75	2.7	2.87	93235221	45.96	52995463	65.81	0.952015	
15.88	15.78	16.23	97934564	48.28	23882096	29.66		Gly/mass
20.81	20.72	20.93	11679628	5.76	3647378	4.53	0.11926	0.1438
PEAK LIST								
GTBE-ANKE-6-4-15(2).RAW								
RT: 2.42 - 3.40								Conversion
Number of detected peaks: 4								41.26%
Apex RT	Start RT	End RT	Area	%Area	Height	%Height	ratio	
2.76	2.68	2.86	47982201	32.81	27746532	48.03	0.636558	
15.87	15.79	16.23	75377552	51.55	23747059	41.1		
16.35	16.29	16.49	17825867	12.19	4646146	8.04	0.236488	Gly/mass
20.79	20.73	20.95	5047916	3.45	1632340	2.83	0.066968	0.0852

Reaction 3: 110°C, 6h, 5%

PEAK LIST

REAGENS-ANKE-20-4-15(2).RAW

RT: 2.50 - 3.34

Number of detected peaks: 3

Apex RT	Start RT	End RT	Area	%Area	Height	%Height	Y	
2.79	2.76	2.9	1.12E+08	42.52	63610967	62.32	0.814054	
15.93	15.83	16.28	1.38E+08	52.23	33975062	33.29		Gly/mass
20.85	20.78	20.96	13872570	5.25	4480472	4.39	0.100572	0.1356

PEAK LIST

GTBE-ANKE-20-4-15(2).RAW

RT: 2.53 - 3.38

Number of detected peaks: 4

Conversion

52.94%

Apex RT	Start RT	End RT	Area	%Area	Height	%Height	ratio	
2.8	2.76	2.88	71017049	30.16	37716038	45.35	0.555717	
15.94	15.84	16.28	1.28E+08	54.27	35218545	42.35		
16.41	16.35	16.54	30478229	12.94	8247889	9.92	0.238496	Gly/mass
20.84	20.79	20.93	6168841	2.62	1983607	2.39	0.048272	0.0631

Reaction 4: 110°C, 6h, 10%

PEAK LIST
REAGENS-ANKE-22-4-15(2).RAW
RT: 2.43 - 3.57
Number of detected peaks: 3

Apex RT	Start RT	End RT	Area	%Area	Height	%Height	Y	
2.82	2.77	2.92	1.14E+08	47.13	64269477	66.97	0.984031	
15.94	15.85	16.3	1.16E+08	47.89	27808953	28.98		Gly/mass
20.86	20.8	20.98	12063858	4.98	3894323	4.06	0.103958	0.1361

PEAK LIST
gtbe-anke-22-4-15(1)02.RAW
RT: 2.44 - 3.67
Number of detected peaks: 4

Conversion
63.23%

Apex RT	Start RT	End RT	Area	%Area	Height	%Height	ratio	
2.87	2.82	2.97	73493835	28	38855457	42.13	0.482464	
16	15.91	16.34	1.52E+08	58.03	43029486	46.65		
16.48	16.41	16.57	30175744	11.5	8386920	9.09	0.198094	Gly/mass
20.91	20.84	21.12	6482517	2.47	1965728	2.13	0.042556	0.0501

Reaction 5: 80°C, 2h, 5%

PEAK LIST								
REAGENS-ANKE-26-3-15(2).RAW								
RT: 0.00 - 26.02								
Number of detected peaks: 3								
Apex RT	Start RT	End RT	Area	%Area	Height	%Height	Y	
2.62	2.57	2.69	71312532	40.17	45376104	61.15	0.733153	
15.75	15.63	16.07	97268252	54.79	26081352	35.15		Gly/mass
20.68	20.59	20.81	8950772	5.04	2741642	3.69	0.092022	0.1017
PEAK LIST								
PRODUCT-ANKE-26-3-15(2).RAW								
RT: 1.09 - 4.28								Conversion
Number of detected peaks: 4								20.32%
Apex RT	Start RT	End RT	Area	%Area	Height	%Height	ratio	
2.61	2.57	2.76	48098466	38.69	28220239	55.94	0.801872	
15.73	15.64	16.11	59982714	48.24	17613494	34.91		
16.21	16.15	16.31	11723326	9.43	3177616	6.3	0.189554	Gly/mass
20.66	20.59	20.87	4526642	3.64	1436659	2.85	0.075466	0.0911

Reaction 6: 110°C, 2h, 10%

PEAK LIST								
REAGENS-ANKE-28-3-15(2).RAW								
RT: 2.31 - 3.35								
Number of detected peaks: 3								
Apex RT	Start RT	End RT	Area	%Area	Height	%Height	Y	
2.63	2.59	2.74	70638569	44.5	40950163	63.82	0.891643	
15.76	15.65	16.1	79222947	49.9	20484939	31.93		Gly/mass
20.69	20.61	20.85	8894178	5.6	2726173	4.25	0.112268	0.1305
PEAK LIST								
PRODUCT-ANKE-28-3-15(1).RAW								
RT: 2.28 - 3.44								Conversion
Number of detected peaks: 4								44.97%
Apex RT	Start RT	End RT	Area	%Area	Height	%Height	ratio	
2.63	2.59	2.76	42045174	28.9	24978953	45.8	0.538405	
15.76	15.66	16.1	78092083	53.68	22503498	41.27		
16.23	16.16	16.37	20634744	14.19	5551026	10.18	0.264236	Gly/mass
20.68	20.6	20.79	4691997	3.23	1500211	2.75	0.060083	0.0756

Reaction 7:110°C, 2h, 5%

PEAK								
LIST								
REAGENS1-ANKE-31-3-15(1).RAW								
RT: 2.37 - 3.31								
Number of detected peaks: 3								
Apex RT	Start RT	End RT	Area	%Area	Height	%Height	Y	
2.63	2.55	2.76	75352830	46.5	44073594	66.19	0.969944	
15.76	15.65	16.15	77687816	47.94	19669778	29.54		Gly/mass
20.7	20.61	20.83	9012771	5.56	2838522	4.26	0.116013	0.1370
PEAK								
LIST								
PRODUCT1(31-3-15)-3-4-15-ANKE(1).RAW								
RT: 2.37 - 3.28								Conversion
Number of detected peaks: 4								37.32%
Apex RT	Start RT	End RT	Area	%Area	Height	%Height	ratio	
2.71	2.63	2.77	39467275	28.99	22174438	44.44	0.546718	
15.84	15.74	16.2	72189509	53.03	21042302	42.17		
16.32	16.25	16.47	19771870	14.52	5170224	10.36	0.273888	Gly/mass
20.76	20.69	20.92	4705801	3.46	1515548	3.04	0.065187	0.0845

Reaction 8: 80°C, 6h, 10%

PEAK LIST								
reagens1-anke-6-5-15(1)02.RAW								
RT: 2.46 - 3.91								
Number of detected peaks: 3								
Apex RT	Start RT	End RT	Area	%Area	Height	%Height	Y	
2.85	2.79	2.98	1.12E+08	41.55	58439462	59.58	0.779865	
15.99	15.89	16.34	1.44E+08	53.28	35293355	35.98		Gly/mass
20.92	20.84	21.04	13948221	5.17	4354690	4.44	0.096948	0.1172
PEAK LIST								
GTBE-ANKE-6-5-15(1)02.RAW								
RT: 0.00 - 26.03								Conversion
Number of detected peaks: 4								35.19%
Apex RT	Start RT	End RT	Area	%Area	Height	%Height	ratio	
3.83	3.78	3.95	33777261	35.43	11363748	45.14	0.662503	
16.99	16.89	17.36	50984332	53.48	11320933	44.97		
17.47	17.4	17.57	7356031	7.72	1781736	7.08	0.14428	Gly/mass
21.98	21.9	22.1	3222506	3.38	708026.9	2.81	0.063206	0.0765

Reaction 9: 80°C, 2h, 10%

PEAK LIST								
REAGENS2-ANKE-31-3-15(2).RAW								
RT: 2.32 - 3.47								
Number of detected peaks: 3								
Apex RT	Start RT	End RT	Area	%Area	Height	%Height	Y	
2.63	2.59	2.75	73148041	44.82	42614248	64.38	0.909821	
15.77	15.66	16.12	80398300	49.27	20550440	31.04		Gly/mass
20.7	20.62	20.82	9448853	5.91	3031432	4.58	0.117526	0.1176
PEAK LIST								
PRODUCT2(31-3-15)-3-4-15-ANKE(2).RAW								
RT: 2.38 - 3.30								Conversion
Number of detected peaks: 4								25.23%
Apex RT	Start RT	End RT	Area	%Area	Height	%Height	ratio	
2.72	2.67	2.82	54314866	32.81%	31339625	49.17	0.639282	
15.85	15.75	16.19	84962246	51.33%	25125739	39.42		
16.33	16.26	16.46	20551083	12.42%	5504313	8.64	0.241885	Gly/mass
20.76	20.7	20.91	5699253	3.44%	1761450	2.76	0.06708	0.0879

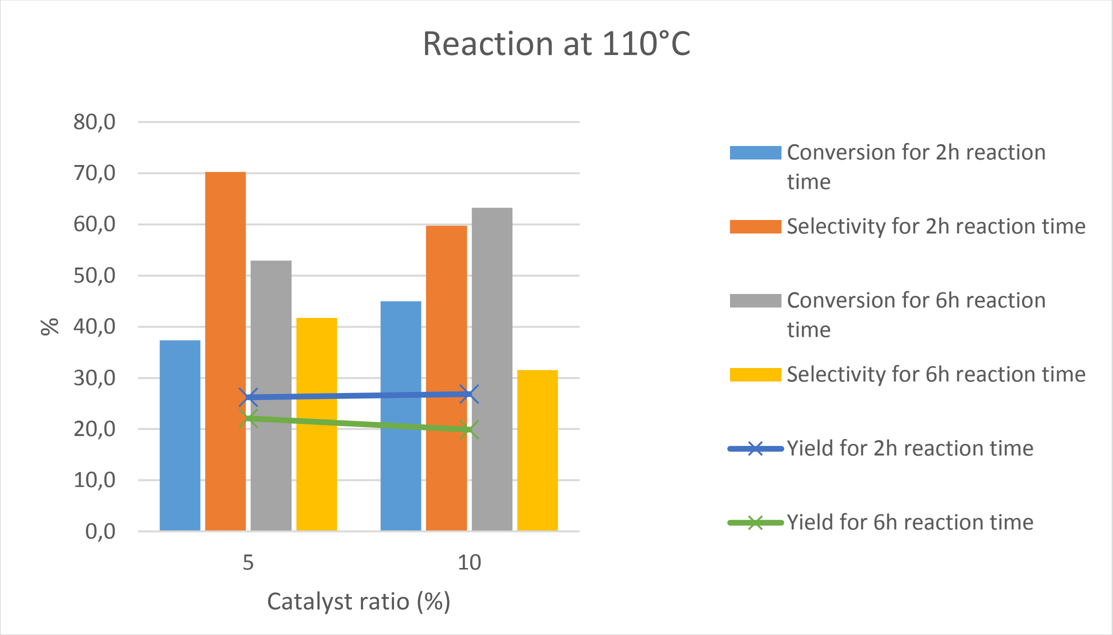
<u>Reaction 10: 95°C, 4h, 7.5%</u>

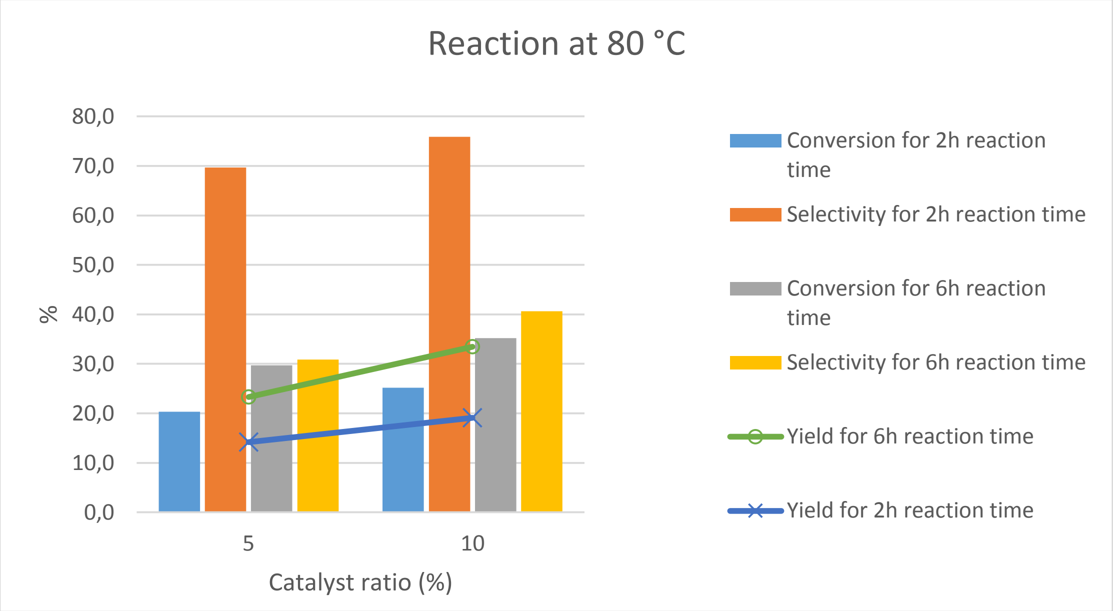
PEAK								
LIST								
REAGENS1-ANKE-8-4-15(2).RAW								
RT: 20.41 - 21.36								
Number of detected peaks: 3								
Apex RT	Start RT	End RT	Area	%Area	Height	%Height	Y	
2.75	2.71	2.85	89592823	42.3	53319051	62.82	0.815314	
15.87	15.77	16.21	1.1E+08	51.89	27640937	32.57		Gly/mass
20.8	20.73	20.94	12307257	5.81	3911404	4.61	0.111999	0.1383
PEAK								
LIST								
GTBE1-ANKE-8-4-15(2).RAW								
RT: 15.69 - 16.95								Conversion
Number of detected peaks: 4								40.29%
Apex RT	Start RT	End RT	Area	%Area	Height	%Height	ratio	
2.75	2.71	2.86	65810377	33.35	38250285	50.84	0.651791	
15.88	15.77	16.27	1.01E+08	51.17	28536519	37.93		
16.36	16.29	16.49	23545793	11.93	6204523	8.25	0.233199	Gly/mass
20.8	20.72	20.91	6979278	3.54	2239276	2.98	0.069123	0.0847

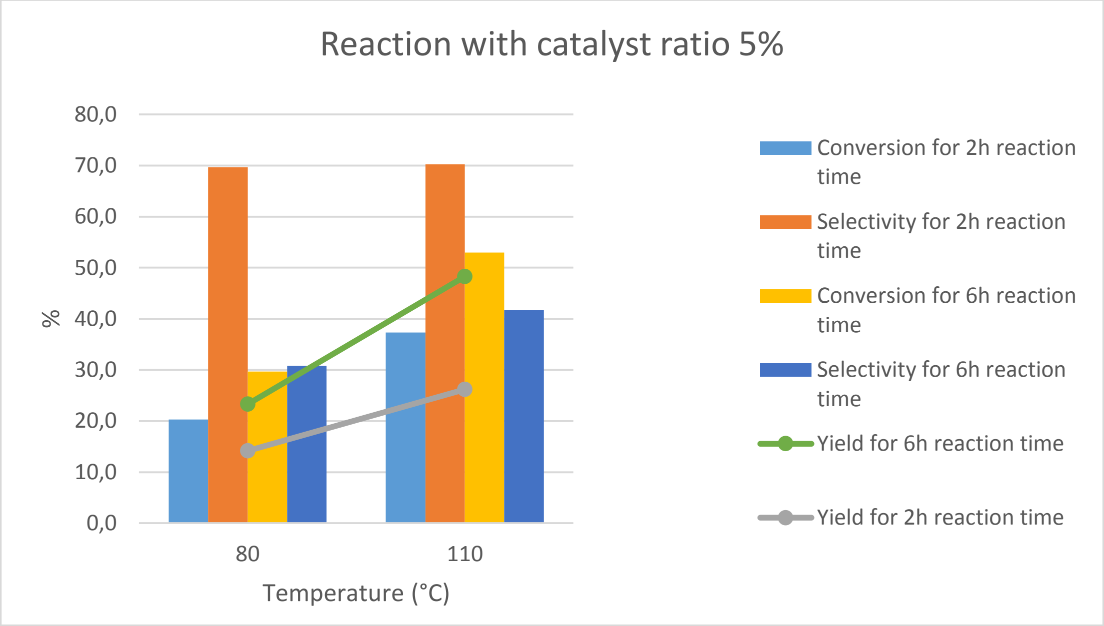
Reaction 11: 95°C, 4h, 7.5%

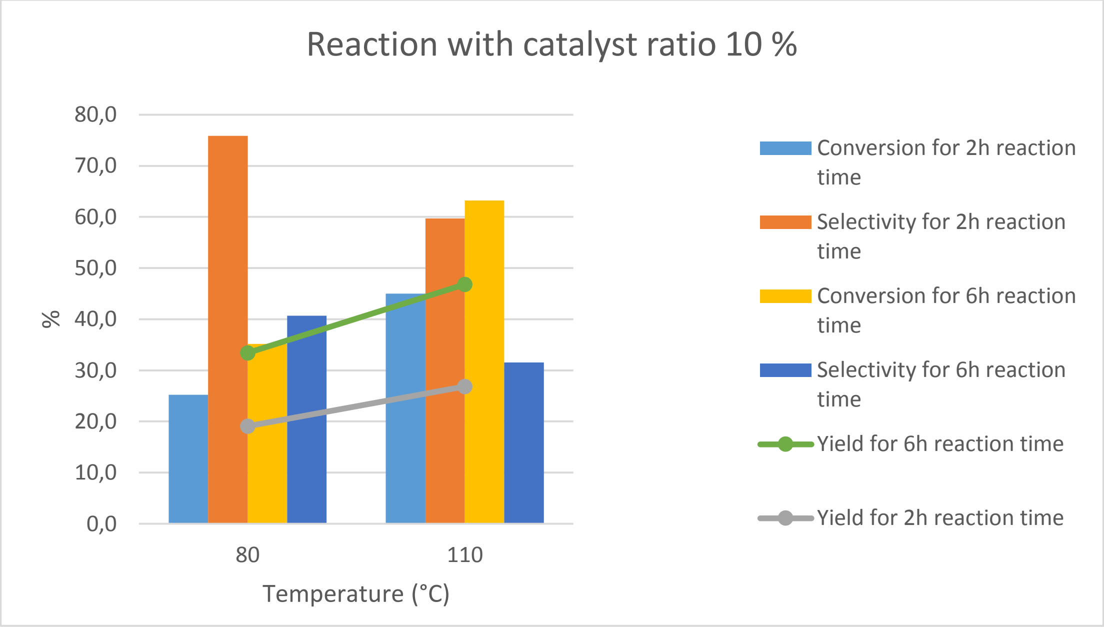
PEAK LIST								
REAGENS-ANKE-23-03-15(2).RAW								
RT: 2.32 - 3.04								
Number of detected peaks: 3								
Apex RT	Start RT	End RT	Area	%Area	Height	%Height	Y	
2.56	2.52	2.7	72631801	44.24	44815232	64.05	0.875885	
15.68	15.57	16.05	82923874	50.51	22407138	32.03		Gly/mass
20.62	20.52	20.74	8623300	5.25	2741565	3.92	0.103991	0.1188
PEAK LIST								
PRODUCT-ANKE-23-3-15(2).RAW								
RT: 2.31 - 3.00								Conversion
Number of detected peaks: 4								41.91%
Apex RT	Start RT	End RT	Area	%Area	Height	%Height	ratio	
2.56	2.52	2.67	40642541	29.02	25684760	47.61	0.531583	
15.69	15.59	16.04	76455707	54.59	21906655	40.6		
16.16	16.1	16.23	11992432	13.78	5181880	9.6	0.156577	Gly/mass
20.6	20.53	20.74	3679994	2.6	1177970	2.18	0.048132	0.0636

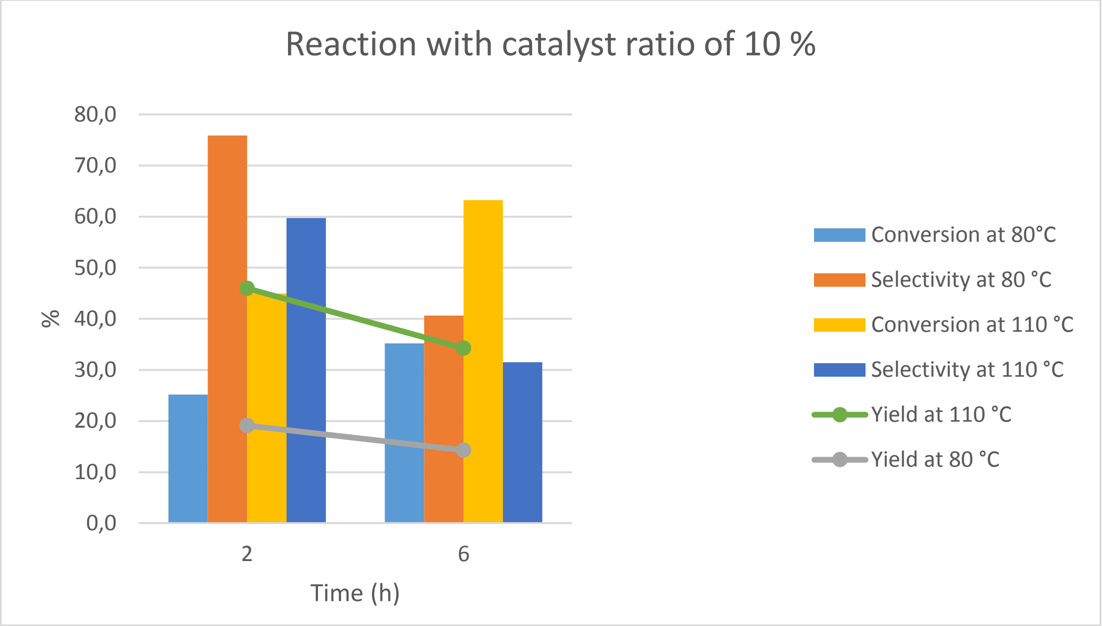
Attachment 5: Extra plots for etherification of glycerol with Beta Zeolite

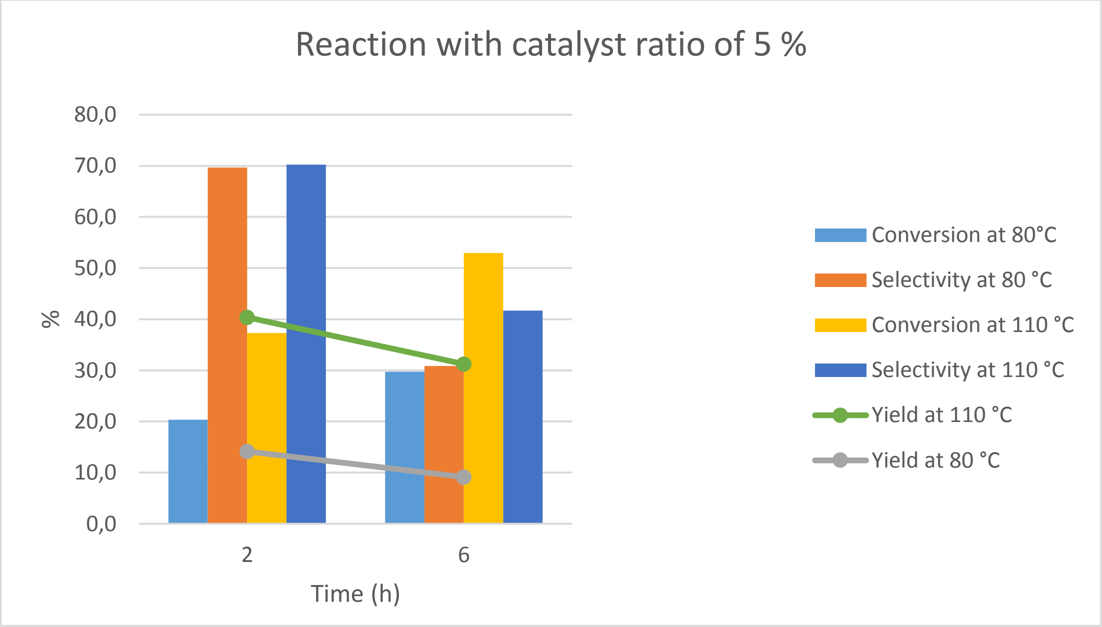





Reaction with catalyst ratio 5%
80,0
70,0
60,0
50,0
40,0
30,0
20,0
10,0
0,0
%
80
110
Temperature (°C)
Conversion for 2h reaction time
Selectivity for 2h reaction time
Conversion for 6h reaction time
Selectivity for 6h reaction time
Yield for 6h reaction time
Yield for 2h reaction time


Reaction with catalyst ratio 10 %
80,0
70,0
60,0
50,0
40,0
30,0
20,0
10,0
0,0
%
80
110
Temperature (°C)
Conversion for 2h reaction time
Selectivity for 2h reaction time
Conversion for 6h reaction time
Selectivity for 6h reaction time
Yield for 6h reaction time
Yield for 2h reaction time


Reaction with catalyst ratio of 10 %
80,0
70,0
60,0
50,0
40,0
30,0
20,0
10,0
0,0
%
2
6
Time (h)
Conversion at 80°C
Selectivity at 80 °C
Conversion at 110 °C
Selectivity at 110 °C
Yield at 110 °C
Yield at 80 °C


Reaction with catalyst ratio of 5 %
80,0
70,0
60,0
50,0
40,0
30,0
20,0
10,0
0,0
%
2
6
Time (h)
Conversion at 80°C
Selectivity at 80 °C
Conversion at 110 °C
Selectivity at 110 °C
Yield at 110 °C
Yield at 80 °C

Attachment 6: Check for outliers and linearity on data conversion and selectivity

a) Conversion

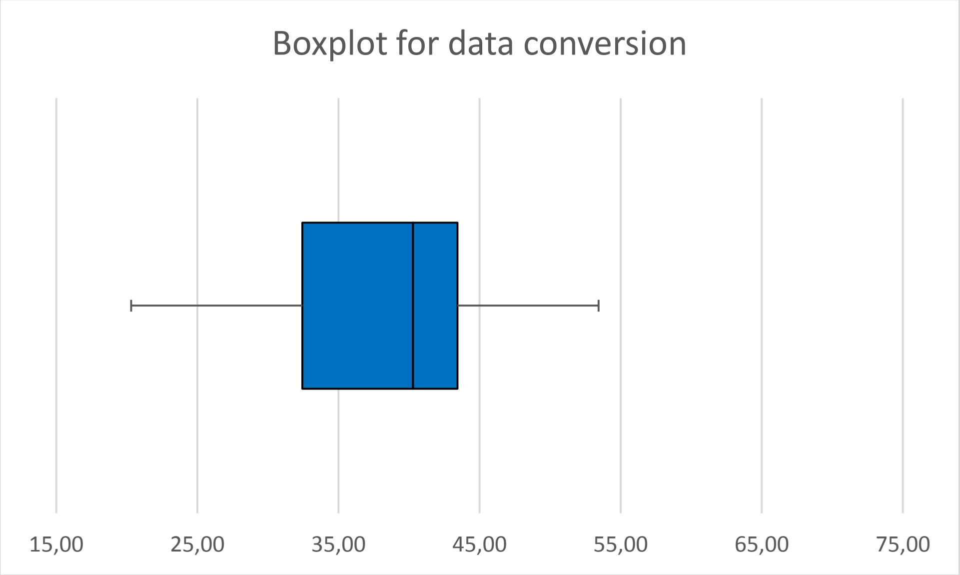


Figure 56: Boxplot for determination of outliers on data conversion

The value of 63.22 can be considered as a mild outlier. However since no other data was present, this value is still used to construct a model for the conversion.

Table 32: f-test for results conversion

	Design points	*Center points*
Mean	38.61	41.15
Variance	208.33	0.67
Observations	8	3
Degrees of Freedom	7	2
F	309.43	
P(F<=f) one sided	**0.0032**	
Critical area of F-test : one sided	19.35	

Table 33: t-test for results of conversion

	Design points	*Center points*
Mean	38.61	41.15
Variance	208.34	0.67
Observations	8	3
Estimated difference between to means	0	
Degrees of Freedom	7	
T- statistical data	-0.50	

P(T<=t) one sided	0.32	
Critical area of T-test: one sided	1.90	
P(T<=t) two sided	**0.64**	
Critical area of T-test: two sided	2.36	

The p-value is higher than 0.05. This implies that the zero hypothesis can be accepted: the design points and center points have equal means, with 95 % confidence.

b) Yield

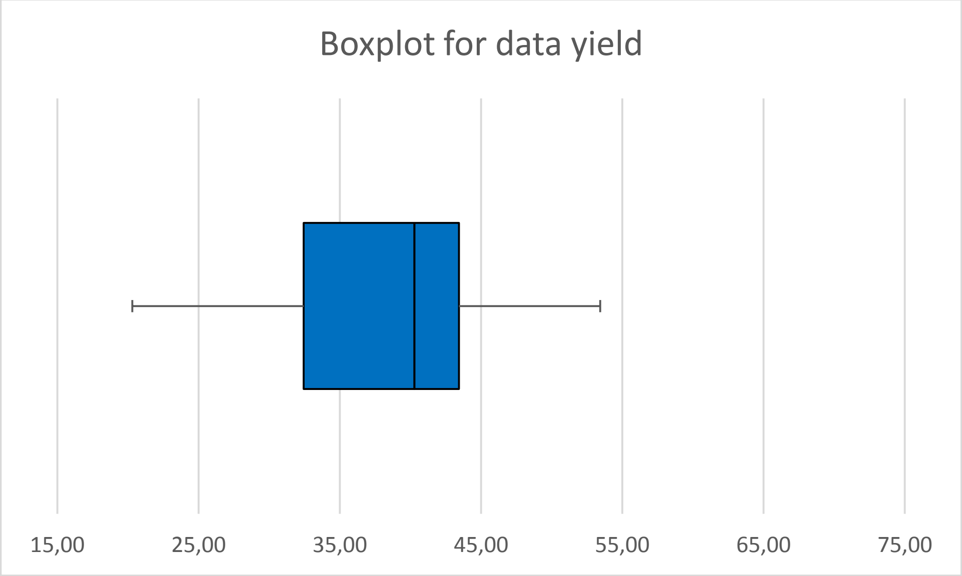


Figure 57: Boxplot for determination of outliers on data yield

From this boxplot, it is clear that no outliers are present.

Table 34: F-test for yield of m-GTBE

	Design points	*Center points*
Mean	18.97	21.39
Variance	38.00	0.10
Observations	8	3
Degrees of Freedom	7	2
F	389.07	
P(F<=f) one sided	**0.0025**	
Critical area of F-test : one sided	19.35	

Table 35: t-test for unequal variances for yield of m-GTBE

	Design points	*Center points*
Mean	18.97	21.39
Variance	38.01	0.10
Observations	8	3
Estimated difference between two means	0	
Degrees of Freedom	7	
T- statistical	-1.11	
P(T<=t) one sided	0.15	
Critical area of T-test: one sided	1.89	
P(T<=t) two sided	**0.31**	
Critical area of T-test: two sided	2.36	

From this t-test, it can be seen that the p-value higher is than 0,05. It can be concluded that the zero hypothesis, which stated that both populations have equal means, is accepted.

Attachment 7: Determination oxygen content

PEAK LIST
Mogas92-2.5%.RAW
RT: 11.62 - 12.75
Number of detected peaks: 2

Apex RT	Start RT	End RT	Area	%Area	Height	%Height	ratio
11.88	11.8	11.99	13043592.5	38.02	4461652	38.74	1.6303
12.37	12.3	12.42	21264994.7	61.98	7055978	61.26	

PEAK LIST
Mogas92-5%.RAW
RT: 11.62 - 12.58
Number of detected peaks: 2

Apex RT	Start RT	End RT	Area	%Area	Height	%Height	ratio
11.88	11.8	12	13026628.2	35.75	4459286	37.99	1.79742
12.37	12.28	12.53	23414349.6	64.25	7278374	62.01	

PEAK LIST
Mogas92-7.5%.RAW
RT: 11.25 - 13.19
Number of detected peaks: 2

Apex RT	Start RT	End RT	Area	%Area	Height	%Height	ratio
11.91	11.85	12.04	436751	30.4	106055.876	26.64	2.28961
12.36	12.3	12.59	999991	69.6	292102.674	73.36	

% m-GTBE	m sample (g)
2.5	0.7836
5	0.7328
7.5	0.793

Conc. M-GTBE (wt%)	Conc. m-GTBE (mg/ml)	Molarity m-GTBE (mol/ml)	Mass oxygen (g)	Oxygen content (%)
2.5	29.7216	0.0002	0.00963	1.22849
5	32.7436	0.00022	0.01061	1.44722
7.5	41.644	0.00028	0.01349	1.70087

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Datum: **10/06/2015**