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Ethers of Glycerol and Isoamylenes as Biodiesel Additives: Synthesis and Characterization

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The influence of reactants, solvents (*tert*-amyl alcohol, dioxane, glyme and diglyme) and temperature on the etherification reaction of glycerol with isoamylenes in the liquid phase catalyzed by a strong acid ion-exchange resin was studied. Reactions were carried out in a batch reactor autoclave at 1.5 MPa in the temperature range from 298 K to 373 K. It has been developed several methods for separation and isolation of products and various techniques of structural characterization (RMN, GC-MS, etc.) have been employed in order to obtain patterns that were used in the calculation of the conversion of glycerol and the composition of the final reaction mixture. It was found that there is a strong temperature influence on the process due to the polarity of employed solvents, resulting in a better conversion of glycerol for the most polar solvent (TAA) at low temperatures (313 K) and in a greater yield of di- and tri-ethers for the less polar solvent (dioxane) at higher temperatures (348 K), leading to different compositions of the products in the final mixture reaction depending on the initial molar ratio of solvents.

1. Introduction

Biodiesel manufacture leads to glycerol as a by-product representing a 10 wt% of the total production causing a surplus in the glycerol market, which value has dropped considerably due to the large increase in biodiesel production during the last decade. Due to its low energy density, high viscosity, and high auto-ignition temperature, glycerol is difficult to burn and it is highly insoluble in diesel fuel, but through chemical modification it can be rendered soluble. European regulations (EC, 2003 and EC, 2009) required that at the end of 2010, the transport fuels should contain 5.83 % of components derived from renewable sources, and establish a 10 % share of energy from renewable sources for transport in the EU energy consumption by 2020. In this context, new components for biodiesel formulation derived from glycerol are currently being investigated.

Some biofuel additives have been developed from etherification of glycerol and isobutene and they have demonstrated to be excellent additives because they improve the properties of fuels while minimizing the emission of toxic substances to the environment (Melero et al., 2010).Closely related to this, there is a feasible analogue process of transforming glycerol into oxygenated derivatives by etherification reactions employing C_5 olefins which would provide very similar properties to biofuels. C_5 olefins, especially Isoamylenes (2-methyl-1-butene and 2-methyl-2-butene), are found in an average composition of 25 wt% in a typical C_5 stream from a Fluid Catalytic Cracking (FCC). These olefins are usually added to gasoline and they are responsible for more than 90 % of the total potential tropospheric ozone formation from gasoline olefins due to their high atmospheric reactivities and Reid vapour pressures (Rock et al., 1992).

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The etherification reaction of glycerol (G) with isoamylenes (iA) consists on three consecutive equilibrium reactions. The reaction products are two monoethers (MTAG's), two diethers (DTAG's) and one triether (TTAG) obtained by etherification of the alcohol groups at positions 1, 2 and 3 of the glycerol (Figure 1).

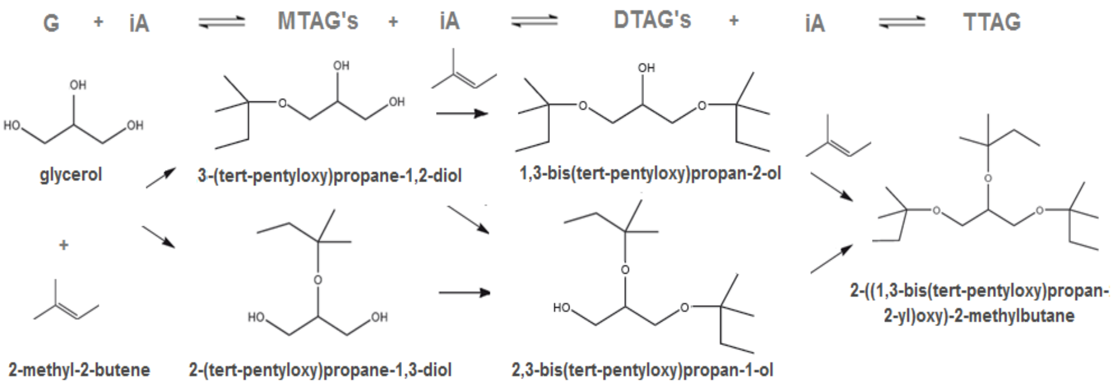

Figure 1: Scheme of the equilibrium reaction system

This reaction occurs in a liquid biphasic system heterogeneously catalyzed by ion exchange resins but it would be possible to perform in one phase this reaction employing solvents. The ethers from glycerol etherification with isoamylenes have not been described in scientific literature, so it was necessary to develop new separation and isolation processes in order to obtain patterns with an appropriate purity for the calculation of conversion of glycerol and selectivities to ethers in the reaction. The aim of this study is to find the best reaction conditions by modifying the molar ratio of the solvent and the reaction temperature. The results obtained will help to give some recommendations that will provide the basis for a novel production process which ensures maximum conversion of glycerol and high selectivity to ethers that would reintroduce and revaluate the glycerol in the biodiesel market.

2. Experimental

2.1 Reagents and catalyst

Glycerol 99.6 % (ACROS), isoamylenes 99 % with a ratio of 90:10 in 2-methyl-2-butene and 2-methyl-1-butene (ACROS) were employed as reactants. Anhydrous dioxane 99.5 % (ACROS), *tert*-amyl alcohol 99 % (Sigma-Aldrich), glyme 99 % (ACROS), diglyme 99 % (ACROS) were employed as solvents. *tert*-Amyl alcohol was also used as reactant considering that it is a potential source of isoamylenes by dehydration of the hydroxyl group in the presence of an acid catalyst resin. Reagent grade solvents were used in the developed isolation and purification processes (water, hexane, diethyl ether, dimethylformamide, methanol and ethyl acetate). Some interesting properties of the employed solvents are listed in Table 1. The solubility of glycerol has been determined in the lab by dissolving 1 g of glycerol in the required amount of each solvent to obtain a single phase.

Table 1: Physicochemical properties of reactants and employed solvents

	tert-Amyl alcohol	Dioxane	Glyme	Diglyme
Relative Polarity (Reichardt, 2003)	> 0.320	0.164	0.231	0.244
Solubility of Glycerol at 298K ($mg_{glycerol}$ / $g_{solvent}$)	Miscible	31	29	21

The catalyst employed in the etherification reaction of glycerol with isoamylenes was a macroporous strong acid ion-exchange resin (Purolite CT275DR). The resin was washed with acetone and air dried at least 24 h, then it was dried into a vacuum oven at 378 K for 8 h under a pressure of 20 mbar.

2.2 Experimental set up and procedure

Reactions were carried out in a 100 mL stainless steel reactor (Autoclave Engineers) pressurized with Argon at 1.5 MPa to ensure the liquid phase over the reaction. The mechanical stirring rate which was found to make negligible the external matter phase transfer effects was 1800 rpm for a reaction time of 24 hours at the temperature range of 298 to 348 K, not exceeding this last value in order to avoid isoamylenes oligomerization (Cruz et al., 2006). Temperature was applied by an external electric heating resistance connected to a Computerized Process Unit (Iberfluid) controlled by internal and external thermocouples. The total reaction volume was 40 mL for a typical equimolar reaction of glycerol and isoamylenes with and without solvents. The amount of solvent employed was expressed in molar ratio and the catalyst was 10 wt% in relation to glycerol. The polar and non polar phases were separated from the final immiscible liquid mixture by decantation, weighing the total amount of each phase just before they were analyzed.

2.3 Isolation and purification of patterns

2.3.1 Isolation

The non-polar phase from reactions of glycerol with isoamylenes was dissolved in hexane and extracted with water in a separating funnel, remaining the glycerol and MTAG’s in the aqueous phase and the DTAG’s and TTAG in the organic phase. The MTAG’s were recovered from the aqueous phase extracting with diethyl ether and this organic phase was then vaporized. The hexane phase from the first extraction was washed with a methanol/water solution (50:50) and then extracted with dimethylformamide, remaining the DTAG’s in the dimethylformamide phase and the TTAG in the hexane phase. The DTAG’s were recovered from the dimethylformamide phase extracting with fresh hexane and both hexane phases were then vaporized. All organic phases were dried with anhydrous magnesium sulphate before the vaporization using a rotatory evaporator.

2.3.2 Purification

After vaporization of the solvents from the organic phases, the total chromatographic signal of the remaining substances was at least 98, 95 and 50 % (arbitrary area units) for MTAG’s, DTAG’s and TTAG respectively. These substances were then purified employing a vacuum distillation process using a Vigreaux column of 10 cm. The pressure was controlled by a vacuum regulator set at 266 Pa engaged to a Torricelli pump. After several vacuum distillation processes, discarding heads and tails for each sample, the final total chromatographic signal of samples was 99.7 % for MTAG’s and 99.5 % for DTAG’s. In the case of TTAG, due to the low purity reached in the extraction and distillation processes, it was necessary to perform a silica gel column chromatography (LC) using hexane/ethyl acetate (97:3) as eluent, resulting in a pattern with a total signal of 99.1 %. All purified samples were assumed as appropriate patterns to evaluate the conversion of glycerol and yield of ethers.

2.4 Analysis and characterization

The corresponding samples from the polar and the non-polar phases were analyzed in a gas chromatograph analyzer Agilent GC7890A, using Helium as gas carrier, with a capillary column HP-Innowax connected to a thermal conductivity detector (TCD) and to a Flame Ionization Detector (FID). The temperature program in GC analysis was set from 313 to 493 K with a slope of 10 K/min and remained constant for 5 minutes at the final temperature. The concentration of the samples in the polar and non polar phase was obtained using an external standard curve determination using the purified patterns.

The samples from patterns of MTAG’s, DTAG’s and TTAG were dissolved in deuterated chloroform and analyzed with a nuclear magnetic resonance spectroscope Mercury 400Q (^{1}H-RMN) and they were also analyzed with a mass spectrometer ThermoFinnigan TRACE DSQ using chemical ionization source (GC-CI/MS).

2.5 Calculations

Conversion of glycerol (X_G) and yields to ethers ($Y_{MTAG's}$, $Y_{DTAG's}$ and Y_{TTAG}) were calculated using the following equations:

$$X_G(\%)=\frac{n_G^0-n_G}{n_G^0}\,x100=\frac{n_{MTAG's}+n_{DTAG's}+n_{TTAG}}{n_G+n_{MTAG's}+n_{DTAG's}+n_{TTAG}}\,x100 \qquad (1)$$

$$Y_{MTAG's}(\%)=\frac{n_{G\rightarrow MTAG's}}{n_G^0}\,x100\;;\;Y_{DTAG's}(\%)=\frac{n_{G\rightarrow DTAG's}}{n_G^0}\,x100\;;\;Y_{TTAG}(\%)=\frac{n_{G\rightarrow TTAG}}{n_G^0}\,x100 \qquad (2)\,(3)\,(4)$$

3. Results and discussion

3.1. Dependence of the solvent

The conversion of glycerol and yields of each product, employing *tert*-Amyl Alcohol (TAA), Dioxane (D), Glyme (GL) and Diglyme (DG) in an equimolar ratio of reactants and solvents, were compared to a reaction without solvent in order to evaluate the influence of the employed solvent at 313 K and at 348 K (Table 2). The final overall composition (wt%) of the mentioned reactions is represented in Figure 2.

Table 2: Evaluation of the type of solvent

Reagents	Molar ratio	T (K)	X_G (%)	Y_{MTAG} (%)	Y_{DTAG} (%)	Y_{TTAG} (%)
R1: G+iA	1:1	348	7.1	1.4	5.4	0.3
R2: G+TAA	1:1	348	0.9	0.5	0.4	0.0
R3: G+iA+TAA	1:1:1	348	5.8	3.5	2.2	0.1
R4: G+iA+DX	1:1:1	348	16.0	13.2	2.6	0.2
R5: G+iA+GL	1:1:1	348	10.9	9.3	1.5	0.1
R6: G+iA+DG	1:1:1	348	10.9	9.9	0.9	0.1
R7: G+iA	1:1	313	2.2	1.8	0.3	0.1
R8: G+TAA	1:1	313	20.3	19.8	0.5	0.0
R9: G+iA+TAA	1:1:1	313	27.3	26.6	0.7	0.0
R10: G+iA+DX	1:1:1	313	9.2	9.1	0.1	0.0
R11: G+iA+GL	1:1:1	313	5.4	5.3	0.1	0.0
R12: G+iA+DG	1:1:1	313	5.9	5.8	0.1	0.0

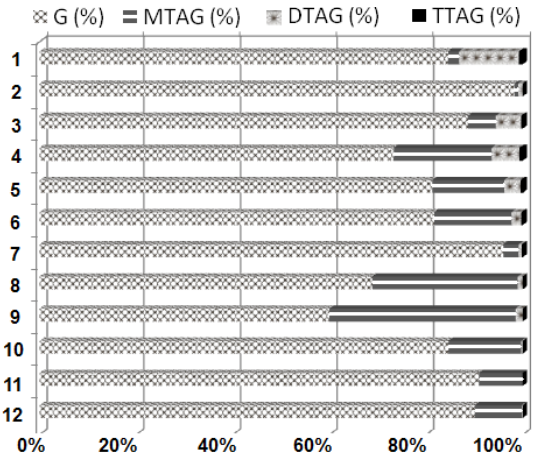

Figure 2: Composition of reactions listed in Table 2

Regardless of the temperature, the etherification reactions of glycerol with isoamylenes without solvent (R1 and R7) provide fewer amounts of ethers but higher selectivities to diethers and triether than reactions using *tert*-amyl alcohol, dioxane, glyme and diglyme. It can be explained by the high insolubility of glycerol into the non polar phase, constituted exclusively by isoamylenes. It seems that in absence of solvent, the limiting step in the reaction system is the formation of MTAG's. It can be argued by the inability of the isoamylenes to solvate the glycerol molecules that can be improved using the appropriate solvents. MTAG's can react efficiently with isoamylenes at high temperature to form DTAG's and in a lesser extent to TTAG. The high steric hindrance of the reaction between DTAG's and isoamylenes can be the reason why the yield of TTAG is so low in all reactions.

The conversion of glycerol and the yield of MTAG's increase when a suitable solvent is employed in the reaction and the greater the solubility of the glycerol in the solvent, the greater the conversion of glycerol and yield of MTAG's achieved. As a general trend, glycerol conversion increases with temperature, showing the same behaviour in reactions with and without solvents. This is due to kinetic considerations but also to the solubility increase of glycerol in the reaction mixture. The reactions which provided the highest conversion of glycerol were R4 at 348 K employing dioxane as solvent and R9 at 313 K using *tert*-amyl alcohol.

3.2. Influence of the molar ratio of solvent

The reactions R4 with dioxane and R9 with TAA were compared to reactions with 0.5, 2, 3 and 4 molar ratio of solvent (Table 3). The final overall composition (wt%) of these reactions is represented in Figure 3.

Table 3: Evaluation of the molar ratio of solvent

Reagents	Molar ratio	T (K)	X_G (%)	Y_{MTAG} (%)	Y_{DTAG} (%)	Y_{TTAG} (%)
R13: G+iA+DX	1:1:0.5	348	6.4	4.5	1.9	0.0
R4: G+iA+DX	1:1:1	348	16.0	13.2	2.6	0.2
R14: G+iA+DX	1:1:2	348	24.5	21.9	2.4	0.2
R15: G+iA+DX	1:1:3	348	25.0	23.0	1.8	0.2
R16: G+iA+DX	1:1:4	348	12.8	12.2	0.6	0.0
R17: G+iA+TAA	1:1:0.5	313	16.1	15.3	0.8	0.0
R9: G+iA+TAA	1:1:1	313	27.3	26.6	0.7	0.0
R18: G+iA+TAA	1:1:2	313	33.8	33.3	0.5	0.0
R19: G+iA+TAA	1:1:3	313	40.9	40.3	0.6	0.0
R20: G+iA+TAA	1:1:4	313	35.2	34.6	0.6	0.0

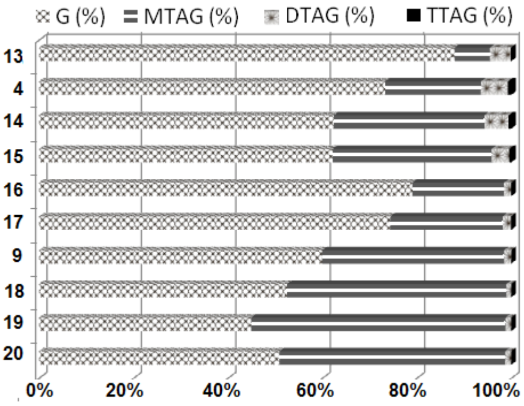

Figure 3: Composition of reactions listed in Table 3

These results indicate that when increasing the molar ratio of the solvent, higher conversion of glycerol and yield of MTAG's are achieved. This is not surprising, because the greater the amount of solvent employed, the greater the amount of glycerol which can react to form MTAG's. However, if the molar ratio of solvent is too high (R16 and R20), lower conversion and yields were obtained due to the lower concentration of reactants, although the reaction occurs in a single phase (R20). As a consequence of the molar ratio of solvent increase, the overall final composition was richer in MTAG's.

3.3. Dependence of the temperature

The temperature dependence was examined at 298, 313, 323, 333 and 348 K for reactions which value of the molar ratio of solvent showed the highest conversion of glycerol at 348 K (R15) and at 313 K (R19). These reactions concurred in the same molar ratio of solvent (1:1:3) and they are compared in Table 4. The final overall composition (wt%) of the mentioned reactions is represented in Figure 4.

Table 4: Evaluation of the temperature dependence

Reagents	Molar ratio	T (K)	X_G (%)	Y_{MTAG} (%)	Y_{DTAG} (%)	Y_{TTAG} (%)
R15: G+iA+DX	1:1:3	348	25.0	23.0	1.8	0.2
R21: G+iA+DX	1:1:3	333	24.8	24.3	0.5	0.0
R22: G+iA+DX	1:1:3	323	16.7	16.5	0.2	0.0
R23: G+iA+DX	1:1:3	313	11.1	11.0	0.1	0.0
R24: G+iA+DX	1:1:3	298	4.8	4.8	0.0	0.0
R25: G+iA+TAA	1:1:3	348	3.7	2.3	1.4	0.0
R26: G+iA+TAA	1:1:3	333	16.2	14.7	1.5	0.0
R27: G+iA+TAA	1:1:3	323	39.5	38.6	0.9	0.0
R19: G+iA+TAA	1:1:3	313	40.9	40.3	0.6	0.0
R28: G+iA+TAA	1:1:3	298	4.8	4.7	0.1	0.0

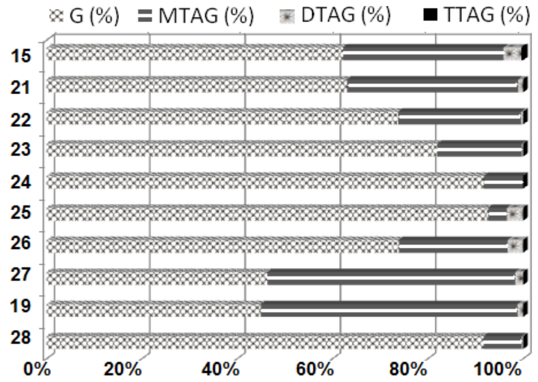

Figure 4: Composition of reactions listed in Table 4

As described before, the temperature exhibits a different trend for dioxane and *tert*-amyl alcohol, resulting in higher conversion of glycerol at higher temperatures when dioxane was the solvent (R15) and at lower temperatures when *tert*-amyl alcohol (R19) was employed as solvent. Nevertheless, the temperature cannot be decreased indefinitely when using *tert*-amyl alcohol, because the reaction rate is greatly reduced in accordance with the kinetics considerations mentioned above. The overall composition of the final mixture shows that MTAG's are formed preferentially over the DTAG's and TTAG using both solvents in the reaction, but their content increased at higher temperatures.

3.4 Influence of water on catalyst performance

In the absence of solvent and when dioxane, glyme and diglyme are employed as solvents, the final mixture contains a small amount of water (<0.95 wt%), independently of the reaction temperature. On the other hand, when using *tert*-amyl alcohol, the water content is dependent of the reaction temperature and a much larger amount of water was detected. The glycerol conversion and the water content were studied as a function of temperature in reactions R25 to R28 and R19, the results are shown in Figure 5.

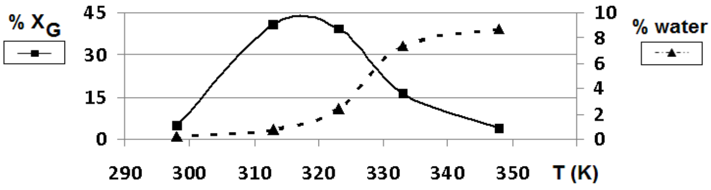

Figure 5: Conversion of glycerol and final water content as a function of the temperature

The conversion of glycerol and the water content in the final mixture show a different behaviour with a temperature increase at temperatures higher than 323 K. It could be due to a competition between the etherification reaction and the *tert*-amyl alcohol decomposition that produces water molecules, which are preferentially adsorbed on the catalyst surface. As a consequence, a substantial decrease on the catalyst activity and hence lower glycerol conversion and lower yields of ethers were obtained.

3.5 Characterization of ethers

The signals of ^{1}H-NMR spectra for 3-(*tert*-pentyloxy)propane-1,2-diol, 1,3-di-*tert*-pentyloxypropan-2-ol (which represent the 98 % and 80 % of the MTAG's and the DTAG's isomer ratio respectively) and 1,2,3-tri-*tert*-pentyloxypropane are described as follows: [3-(*tert*-pentyloxy)propane-1,2-diol] = ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.83 – 3.76 (1H, m, C*H*OH), 3.71 (1H, dd, *J* = 11.4, 3.9 Hz, CH_2OH), 3.64 (1H, dd, *J* = 11.4, 5.2 Hz, CH_2OH), 3.47 – 3.37 (2H, m, CH_2OC), 2.97 (2H, br. s, O*H*), 1.50 (2H, q, *J* = 7.5 Hz, CH_2CH_3), 1.14 (6H, s, 2 × CCH_3), 0.87 (3H t, *J* = 7.5 Hz, CH_2CH_3); [1,3-bis-*tert*-pentyloxypropan-2-ol] = ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.87 – 3.74 (1H, m, C*H*OH), 3.43 – 3.31 (4H, m, 2 × CH_2OC), 2.59 (1H, br. s, O*H*), 1.49 (4H, q, *J* = 7.5 Hz, 2 × CH_2CH_3), 1.13 (12H, s, 4 × CH_3C), 0.86 (6H, t, *J* = 7.5 Hz, 2 × CH_2CH_3); [1,2,3-tri-*tert*-pentyloxypropane] = ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.69 – 3.54 (1H, m, C*H*OC), 3.33 (2H, dd, *J* = 8.8, 5.9 Hz, CH_2OC), 3.23 (2H, dd, *J* = 8.9, 5.3 Hz, CH_2OC), 1.54 – 1.41 (6H, m, 3 × CH_2CH_3), 1.14 (6H, s, 2 × CCH_3), 1.10 (12H, s, 4 × CCH_3), 0.92 – 0.83 (9H, m, 3 × CH_2CH_3).

The GC-CI/MS spectra of the ethers are illustrated in Figure 6, emphasizing the molecular weight.

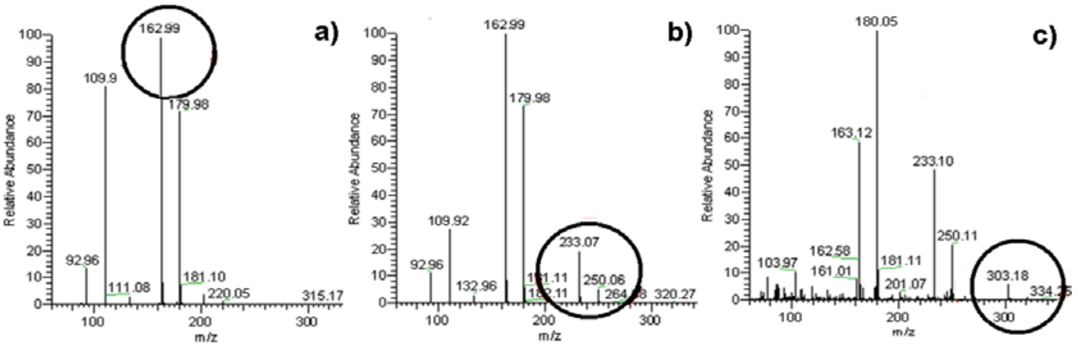

Figure 6: GC-CI/MS spectra of MTAG (a), DTAG (b) and TTAG (c)

4. Conclusions

The etherification reaction of glycerol with isoamylenes, the identification and characterization of the ethers related was successfully carried out. The best early conditions for a feasible industrial process, in order to revaluate glycerol by etherification with isoamylenes, were achieved with the use of *tert*-amyl alcohol as solvent at 313 K due its total miscibility with glycerol, the lower formation of water and the consequent higher conversion of glycerol. In this reaction, the polarity of solvent is the responsible of that MTAG's were the main products obtained, but the influence of the initial ratio of reactants should be explored in order to improve the glycerol conversion and yields of the DTAG's and TTAG.

Acknowledgements

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