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Developing *N*-alkylated fatty amines based on glycerol-derivable building blocks.

A path towards renewable surface active molecules.

Degree project report in Materials Chemistry

Martina Zarowiecki

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2026
www.chalmers.se

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Supervisor: Petter Dunås, Nouryon Stenungsund, product chemistry
Examiner: Nina Kann, Department of Chemistry and Chemical Engineering

Degree project report 2026
Department of Chemistry and Chemical Engineering
Chalmers University of Technology
SE-412 96 Gothenburg
Sweden
Telephone +46 31 772 1000

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Abstract

Nouryon is a leading company in specialty chemicals and a pioneer in surface active molecules. One of its key product classes is nonionic surfactants, widely used in agriculture, personal care, oilfield and more. Currently, Nouryon produces alkoxylated nonionic surfactants, where the hydrophilic headgroup is based on epoxides sourced from fossil raw materials. Alkoxylated amines are paticulary important in agriculture, where they serve as effective adjuvants in glyphosate based herbicides. Due to environmental concerns and the interest in fully bio-based alternatives to alkoxylated surfactants, alternative synthetic routes and starting materials for the hydrophilic headgroup is being investigated in this study. One readily available bio-based material which could act as a good alternative to epoxides is glycerol. In this study, alternative synthetic routes based on glycerol derivable building blocks are being investigated with the intention of producing fully bio-based nonionic sufactants, focusing on the *N*-alkylation of fatty amines. The synthesis is conducted in labscale and evaluated with NMR and GC-MS/FID.

The results showed that reacting glycerol carbonate and fatty amines with catalyst such as $Ca(OH)_2$, MgO or ZnO, at temperatures above 190 °C yielded significant amount of alkylated products such as *N*-alkyl serinol carbamates, 2,3-dihydroxypropyl amines and bis-2,3-dihydroxypropyl amines. While total amount of alkylation was similar across catalyst, $Ca(OH)_2$ resulted in higher yields of both 2,3-dihydroxypropyl amines and bis-2,3-dihydroxypropyl amines. Under one set of optimized conditions (2 eq. glycerol carbonate, 0.3 eq. $Ca(OH)_2$ and 1 eq. of fatty amine, 220 °C, 6h.), 86 % yield of alkylated product was reached. Additionally, doing a onepot synthesis starting with readily available materials such as urea and glycerol instead of glycerol carbonate, resulted in less selectivity towards alkylated products. For both approaches, the reaction showed to be heavily shifted towards *N*-alkyl serinol carbamates, which limits formation of bis-2,3-dihydroxypropyl amines. The yield of 2,3-dihydroxypropyl amines could be increased by base hydrolysis of N-alkyl serinol carbamates. Based on these findings, by applying the optimized conditions, it is possible to attach a hydrophilic headgroup with a hydrophobic tail from sources that could be derived from renewable materials with this chemistry. The hydrophilic headgroup could be based on polyglycerol carbonates derived from recycled and bio-based CO_2 or urea and polyglycerol. The hydrophobic tail could be based on fatty amines derived from either tallow or coconut.

Keywords: Nonionic surfactants, glycerol, biobased, alkoxylated amines.

Acknowledgements

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Martina Zarowiecki, Gothenburg, February 2026

List of Acronyms

Below is the list of acronyms that have been used throughout this thesis listed in alphabetical order:

cat	Catalyst
CD_3OD	Deuterated methanol
$CDCL_3$	Deuterated chloroform
EO	Ethylene oxide
eq	equivalent
FA	Fatty amine
GC	Glycerol carbonate
gHSQCAD	Gradient heteronuclear single quantum coherence with adiabatic pulses and differentiation
GC-MS/FID	Gas chromatography with mass spectrometry and flame ionization detector
GBH	Glyphopsate based herbicide
MSTFA	*N*-Methyl-*N*-trimethylsilyl trifluoroacetamide
NMR	Nuclear magnetic resonance
POEA	Polyethoxylated tallow amine
TMCS	Trimethylchlorosilane
WRT	With respect to

Nomenclature

Below is the variables that have been used throughout this thesis.

Variables

r_i	Reaction rate for reaction i
a_j	Area from ^{1}H NMR for proton environment a for molecules $j = I - VIII$
b_j	Area from ^{1}H NMR for proton environment b for molecules $j = I - VIII$
c_k	Area from ^{1}H NMR for proton environment c for molecules $k = I, II, VIII$

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1
Introduction

This thesis was conducted at Nouryon Surface chemistry R&D facility in Stenungsund, as part of the Surf To Green project, which aims to develop bio-based surfactants based on biomass sourced from agriculture and forest side-streams. Currently, Nouryon produces a range of surfactants, including ethoxylated amines, which can be used in a range of applications such as demulsifiers in oilfield applications [1], and in agriculture as a corrosion inhibitor, chemical intermediate, adjuvant and emulsifiers [2]. One such ethoxylated amine is polyethoxylated tallow amines (POEAs), which have historically been used as adjuvants in glyphosate based herbicides (GBHs). Studies have shown that including POEAs in GBHs formulations increases toxicity leading to significant aquatic toxicity [3] and effect on human health [4]. According to previous research published in 2019, GBHs formulations containing POEAs have systematically been replaced with ethoxylated ether amines or propoxylated quaternary ammonium surfactants in the EU, which are considered to exhibit lower toxicity in GBHs formulations [4]. However, POEAs in GBHs are still being used in the US (2019).

What all alkoxylated products share in common, are their hydrophilic head group, which is most commonly based on epoxides sourced from fossil raw materials. The hydrophobic tail can be derived from biobased materials. The environmental degradation of alkoxylated surfactants synthesized from fossil-based feedstocks results in the formation and release of greenhouse gases, thereby intensifying the atmospheric greenhouse effect and contributing to global warming. Due to growing concerns regarding climate change, the environmental impact of synthetic surfactants and the demand for fully bio-based products have led to the need to explore fully renewable alternatives to epoxides, such as glycerol. Glycerol is a readily available bio-based raw material, which is highly polar, water soluble and available in large amounts as a side product from the production of fatty acids and esters from fats. Glycerol can be used to synthesize glycerol carbonate (GC) with urea or CO_2. Urea can be synthesized from ammonia and carbon dioxide, which are both gases commonly produced as side products in industrial synthesis. Nouryon currently already has the capacity and infrastructure of storing up to 5000 ton ammonia at their facility in Stenungsund [5].

This thesis focuses on the *N*-alkylation of fatty amines (FA) with glycerol-derived building blocks as a platform for the development of nonionic surfactants. The focus will be on the development and optimization of the alkylation of FA with GC or glycerol and urea in lab scale. No application test or surface activity was investigated. The chemistry is explored with the perspective of enabling the synthesis of

polyglycerol FA, which represent a promising class of nonionic surfactants derived from bio-based feedstocks. While the FA employed in this work are not bio-based, the methodology established herein provides a foundation that could be directly applied to bio-based nonionic surfactants in future studies.

1.1 Background

Previous research groups have investigated the synthesis of serinol carbamates from glycerol and urea or GC and urea, Figure 1.1.

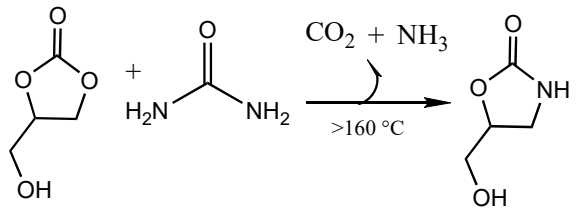


Figure 1.1: Reaction scheme between GC and urea above 160 °C [6].

According to Dibenedetto et. al (2012) [6], at temperatures above 160 °C, urea will quickly decompose to ammonia and isocyanic acid, Figure 1.2.a). The ammonia will then react with the GC, creating carbamates, Figure 1.2.b).

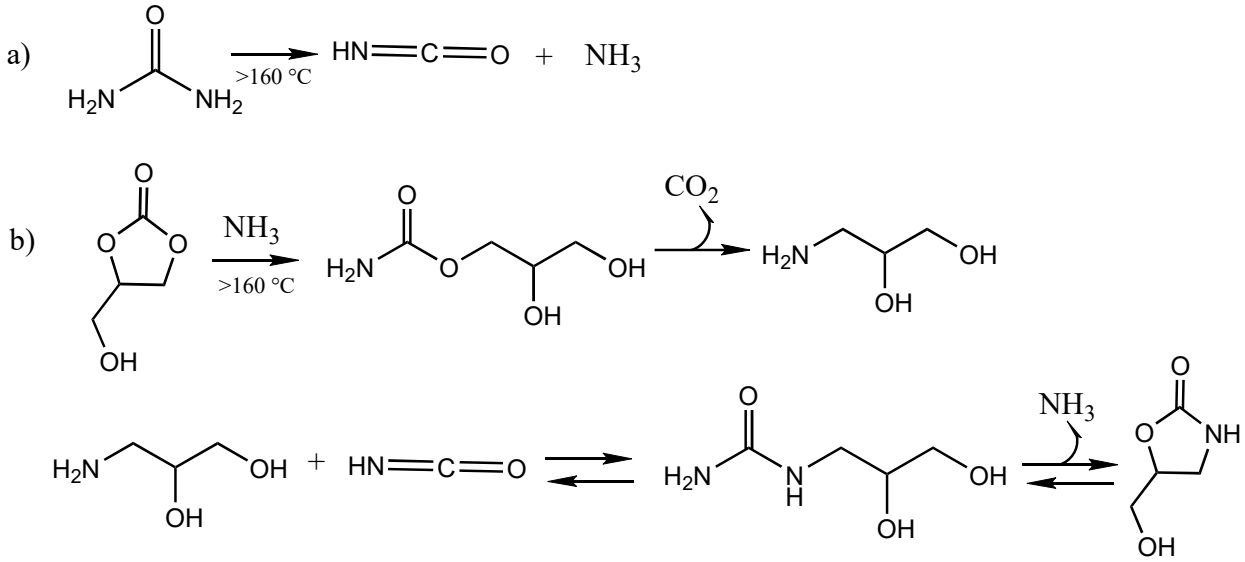


Figure 1.2: Reaction mechanisms between GC and urea at temperatures above 160 °C [6].

At these temperatures, the carbamate can decompose into three different paths, Figure 1.3. 1. it could decompose into glycerol and isocyanic acid, 2. it could lose ammonia to afford GC and 3. it could decompose into carbon dioxide and serinol. If decomposition path 3 continues, serinol carbamates could be afforded according to the proposed reaction mechanism in Figure 1.2.

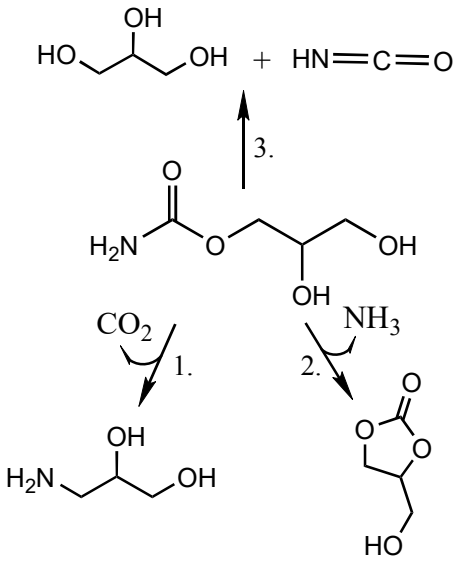


Figure 1.3: Different reaction pathways the decomposition of carbamates can take [6].

In the last step in the reaction scheme in Figure 1.2, where serinol carbamates are formed, removal of ammonia pushes the equilibrium towards the desired serinol carbamate. This observation suggests that the last step is also an equilibrium reaction.

Another group have looked into similar reactions with the intention to react ethylene glycol and urea, making carbamates that will degrade into ethylene carbonate. What these studies showed was that catalyst with increasing basic properties, increased its selectivity towards serinol carbamate [7]. However, the yield of ethylene glycol was still high (66-85 %). Some of the catalyst tested, where CaO, MgO and ZnO, which basicity goes from highest for CaO to the lowest for ZnO. Additionally, another group examined the synthesis of serinol from a 2 step reaction using glycerol or GC and urea, where serinol carbamates was initially produced, following a hydrolysis procedure, where the serinol carbamate intermediate is hydrolyzed into serinols. This group used for instance MgO as their catalyst.[8].

Furthermore, previous studies have shown that GC in the presence of strong basic catalyst [9] can yield glycidol via anionic ring opening reactions [10], Figure 1.4a). According to Pan et. al (2012) [11], when reacting glycerol and dimethyl carbonate in the presence of basic catalysts such as CaO, the selectivity towards glycidol is 25 % whilst the rest is GC. Additionally, weaker alkaline catalyst such as MgO was also tested, which did not yield any glycidol. When glycidol is formed, it can react with fatty amines yielding 2,3-dihydroxypropyl amines and bis-2,3-dihydroxypropyl amines, Figure 1.4b).

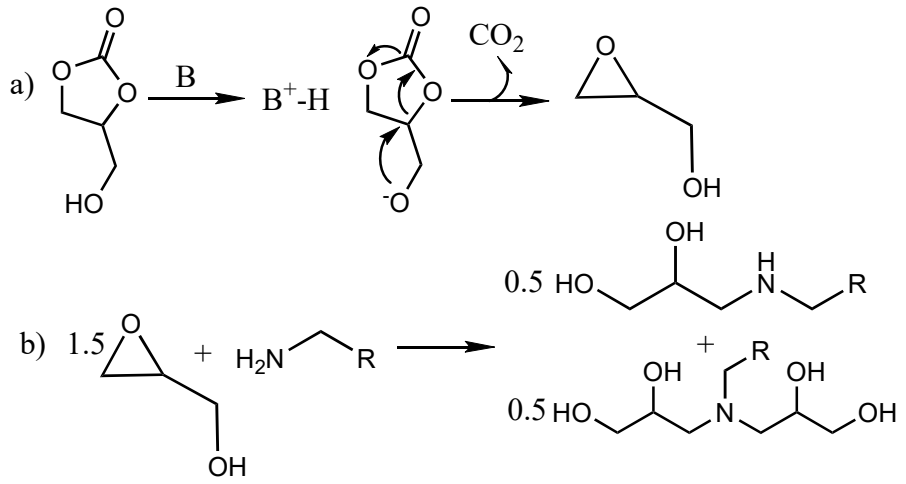


Figure 1.4: a) Decomposition of GC in the presence of a basic catalyst [10] b) Reaction between glycidol and a primary FA [12].

In the previous research presented, ammonia could act as a nucleophile attaching itself to GC. By exchanging the ammonia with a fatty amine, this thesis evaluates the synthesis of serinol and serinol carbamate derivatives with long aliphatic chains, as a way to make bio-based surface active molecules.

2
Theory

2.1 Ethoxylation of FA

Nonionic surfactants are a class of surface active molecules consisting of a hydrophilic head group and a hydrophobic tail. Many nonionic surfactants are made via alkoxylation, where epoxides are added to other compounds. One type of alkoxylations is ethoxylation of FAs, were ethylene oxide (EO) and FA could be reacted at elevated temperatures. For ethoxylation of FA, the ethoxylation degree is highly temperature dependent. Without catalyst, 2 moles of EO could be added at 230 °C, whilst at 120 °C and 90 °C, 4 and 10 moles of EO could be added [12]. Suggesting that lower temperatures favours higher ethoxylation degrees. When adding 0.05% alkaline catalyst such as NaOH to the reaction at 230 °C, the reaction rate and the degree of ethoxylation could be increased significantly.

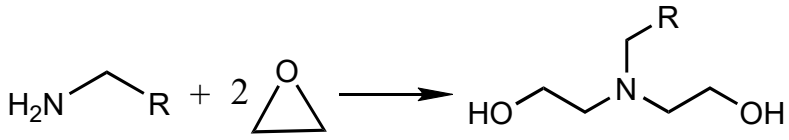


Figure 2.1: Reaction scheme for ethoxylation of FA with EO [13].

The amount of EO in the ethoxylated product determines its solubility in water, with surfactants with increasing EO units being able to more effectively lower the surface tension of water [14]. EO is currently sourced from fossil raw materials and poses several risks for human health, aquatic life and more.

2.2 Starting materials for bio-based surfactants

Nouryon currently produces biobased FA from sources such as tallow (16C-18C) [4] and coconut (12C-14C) [15] in their product line Armeen [16, 17, 18, 19]. FA can be produced from fatty acids with an excess of ammonia and nickel or cobalt catalyst [20]. Initially, ammonia will react with the fatty acid forming nitriles and water. This step is followed by the hydrogenation of nitriles, forming FA.

Glycerol is a large side-product from transesterfication of triglycerides from fats with alcohol in the presence of a catalyst such as NaOH and KOH. Glycerol and polyglycerols can be used to produce GC with CO_2 and glycerol [21] or urea and

glycerol [7]. Urea can be synthesized via the Bosch–Meiser process, where ammonia and CO_2 are used as starting materials [22]. Ammonia is mainly produced through the Haber-Bosch process and could be fully bio-based by reacting green hydrogen from electrolysis with nitrogen gas separated from air. However, the Haber Bosch process consumes an immense amount of energy and is dependent on green hydrogen production to make this process sustainable and biobased. Alternatives to the Haber Bosch process is the electrocatalytic nitrogen reduction reaction, where water is used as the hydrogen source and the process consumes less energy [23]. However, this reaction still suffers from low yields.

2.3 Gas chromatography (GC-MS/FID)

Gas chromatography is a chromatographic technique utilizing chemically inert gas as the mobile phase and liquid or solid as the stationary phase. This method can analyze products that can vaporize without decomposition. The sample is vaporized and transported through the column in the mobile gas phase. Depending on the compounds affinity to the stationary phase, the analytes will move through the column faster/slower, which is how analytes are separated in this method. Attached to a gas chromatography column, is a detector which could analyze the molecule semi quantitatively or qualitatively. Many gas chromatography instruments combine different detectors, such as flame ionization detector (FID) and mass spectrometry (MS) detector. The purpose of combining an MS detector and an FID, is to get both a semi-quantitative and qualitative analysis of the compound [24].

In a MS detector, the sample is ionized and fragmented by an ion source. Each type of fragment is linked to a specific compound by a unique mass to charge ratio. This gives a qualitative analysis of the product. FID are mass sensitive and will detect the relative mass of organic vapor in the carrier gas. The FID will create a flame with the sample, creating ionized compounds. A voltage will be applied over the flame, yielding a current, which magnitude is linked to a specific compound and its amount.

2.4 Nuclear magnetic resonance spectroscopy (NMR)

NMR spectroscopy detects atomic nuclei and the environment its in within the molecule. This method could be used to both qualitatively and quantitatively identify compounds. The NMR instrument consist of a magnet, which will expose the nuclei in an atom to a strong magnetic field. For the nuclei to interact with the magnet, it needs to be magnetic itself, meaning it needs to have nucleus spin. When the nucleus is spinning and interacts with an external magnetic field, it can align itself with the magnetic field, which is the lowest energy state, or against the field which is the highest energy state. By applying a stronger magnetic field, the energy difference between the lowest and the highest energy state will be increased. By applying a short pulse of radio frequency, some nuclei will absorb the energy and will be promoted to the higher energy state. When the nuclei returns to the lowest

energy state, the energy corresponding to the difference in energy between lower and higher state, will be released in the form of radiation that will be detected.

Since the difference in energy is quantified and specific for different nuclei environments, it will give a signal characteristic for an atom in a specific environment. In proton and carbon atoms, the ^{1}H and ^{13}C isotopes are magnetic and will interact with the magnet [25]. gradient Heteronuclear Single Quantum Coherence with Adiabatic pulses and Differentiation (gHSQCAD) is a 2D-NMR spectroscopy method that correlates two different types of nuclei, which couples protons that are directly attached to a carbon [26].

3
Experimental

3.1 Synthesis

All trials were conducted at laboratory scale, either in 100 mL three necked round-bottom flasks equipped with condensers and operated under open atmosphere conditions, or in vial reactors open to the atmosphere via septum needles. The reactors were placed on temperature controlled heating blocks, and a magnetic stirring bar was added directly to each reaction mixture to ensure continuous stirring. The specific reaction conditions, durations, and materials for each experiment are listed in section A.4. To prevent overflow caused by gas evolution, all reactions were heated gradually.

3.2 Characterization methods

To qualitatively and quantitatively characterize the products, NMR and GC-MS/FID were used as analytical tools. NMR was mostly used for analysis, where chemical shifts in ^{13}C and ^{1}H NMR for molecules I-V and VII-VIII was determined by producing references and additionally validating some of the products with GC-MS/FID analysis. The yield is based on the FA starting material and could be quantified by ^{1}H NMR. GC/MS-FID was also used for a few selected reactions.

3.2.1 Nuclear magnetic resonance (NMR)

NMR spectras were recorded in a Varian 400 MHz NMR spectrometer. NMR samples were prepared by adding the sample and 50:50 vol% of deuterated methanol (CD_3OD) and deuterated chloroform ($CDCl_3$) to a NMR vial. ^{1}HNMR, ^{13}C and gHSQCAD were used to determine components both qualitatively and quantitatively. The main products for this thesis was 2,3-dihydroxypropyl *N*-alkylcarbamate (IV), *N*-alkyl serinol carbamate (III), 2,3-dihydroxypropyl amines (II) and Bis-2,3-dihydroxypropyl amines (I), see Figure 3.1.

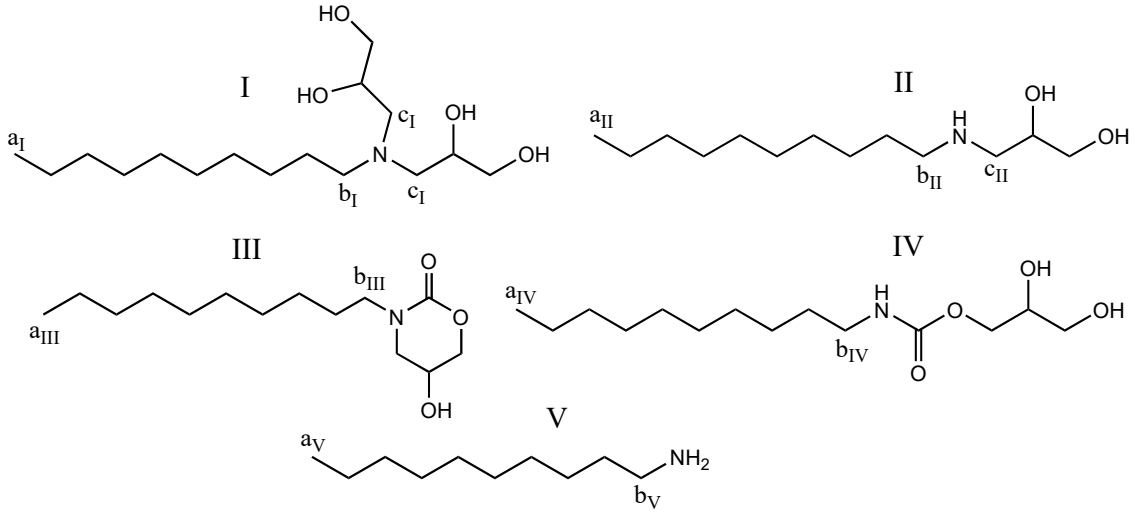


Figure 3.1: These molecules are the main products from reacting GC or glycerol and urea with primary FAs and will be referred to in the NMR and GC-MS/FID results.

Molecule I, II, III, IV and V are detectable in ^{1}HNMR, where the proton environment b in molecule I, II and V, see Figure 3.1 are shifted upfield around 2.5 ppm as opposed to molecules III and IV, which are shifted downfield at around 3.2 and 3 ppm. The methyl group from the FA acts as an internal standard. By integrating the resulting peaks in ^{1}H NMR spectra, the yield based on the FA can be determined. Based on ^{1}H NMR, from reacting GC, primary FA and catalyst, the yield of IV and III could be determined via integrals $A = b_{III}$ and $B = b_{IV}$. The integrals are for the two protons in environment b, so to get the yield of molecule III and IV respectively, the integrals are divided by two, Figure 3.2.

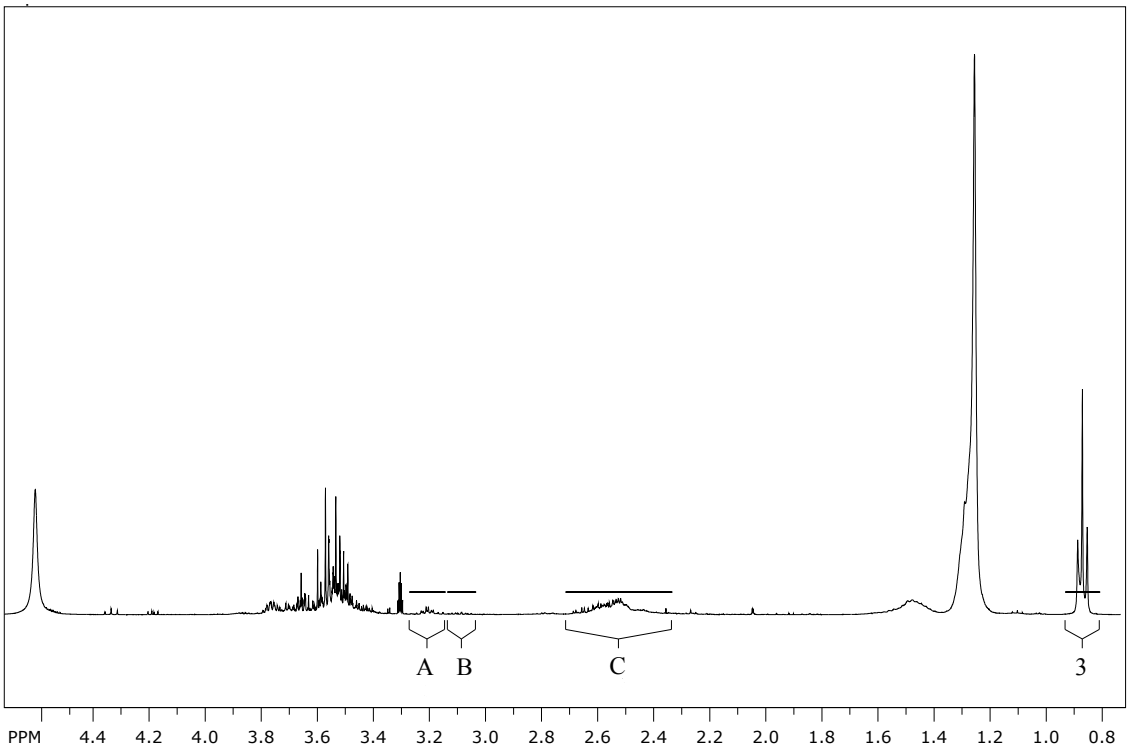


Figure 3.2: This is a typical ^{1}H NMR spectrum from the reaction of GC and FA resulting in products I-IV.

The yield of 1 molecule II and 2 molecule I can be determined by assuming that the only products yielded from FA, molecule V are molecules I-V. This gives the sum of 2 when accounting for the protons in environment b, for molecule I-V, see Equation 3.1, representing 2 protons from environment b in Figure 3.1. If the FA reacts into other products than I-V, the model will become less accurate.

$$2 = b_I + b_{II} + b_{III} + b_{IV} + b_V \tag{3.1}$$

In area C, several peaks from molecules I, II and V could be detected seen in Equation 3.2. By inserting Equation 3.1 in Equation 3.2, the sum of 2 protons from c_{II} and 4 protons from c_I can be determined, by dividing this sum by 2, the yield of 1 equivalent molecule II and 2 equivalents molecule I could be determined, according to Equation 3.3. This means that the yield of molecules II, will be weighted, meaning that if the product contains molecule II, there will be an overestimation of the total amount of alkylated products.

$$C = b_I + 2c_I + b_{II} + c_{II} + b_V \tag{3.2}$$

$$Yield\ 1\ eq.\ II\ \&\ 2\ eq.\ I = \frac{A + B + C - 2}{2} = \frac{c_{II} + 2c_I}{2} \tag{3.3}$$

When reacting GC and secondary FA with a catalyst, the products will instead be a carbamate molecule VII, 2,3-dihydroxypropyl dialkylamines (VIII) and unreacted FA (VI), see Figure 3.3.

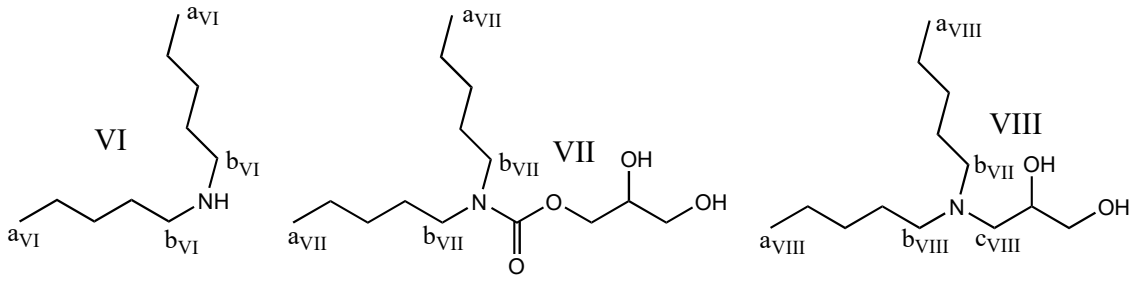


Figure 3.3: These molecules are the main products from reacting GC and secondary FA and will be referred to in the NMR results.

Similarly, the yield of VII can be determined from area D, since $D = 2b_{VII}$. Since peak D contains 4 protons from environment b, to get the yield of molecule VII, area D needs to be divided by 4. Peak E contains both peaks from molecule VI and VIII, see Figure 3.4.

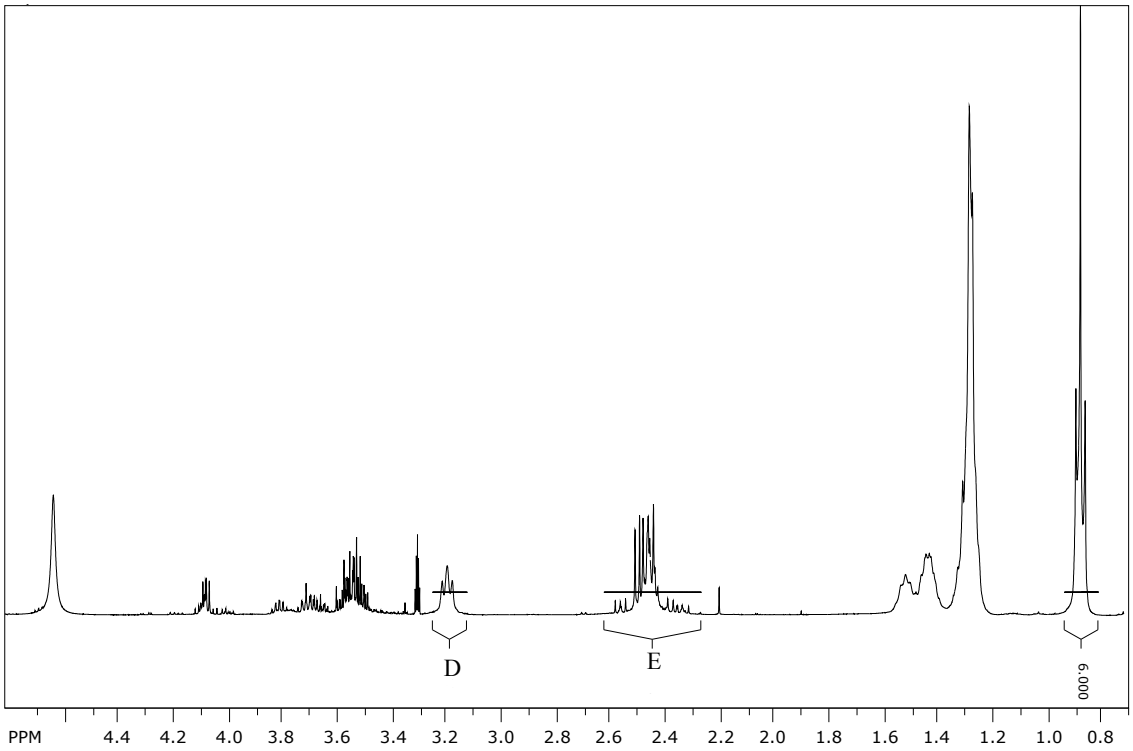


Figure 3.4: This is a typical ^{1}H NMR from reacting GC and secondary FA resulting in products VI-VIII.

The yield of VI and VIII can be determined, respectively, by assuming that molecule VI-VIII are the only yielded products containing the FA starting material. The sum of the protons in environment b should be 4, see Equation 3.4. In area E, peaks from environment b for VI and VIII and environment c in VIII are detected according to Equation 3.5.

$$4 = 2b_{VI} + 2b_{VII} + 2b_{VIII} \tag{3.4}$$

$$E = 2b_{VI} + 2b_{VIII} + c_{VIII} \tag{3.5}$$

By inserting Equation 3.4 in Equation 3.5, one can determine c_{VIII}. Since c_{VIII} represents 2 protons in environment c, the yield for molecule VIII is determined by dividing c_{VIII} with 2, Equation 3.6. By knowing the yield of VIII, the yield of VI can be determined aswell, since $c_{VIII} = b_{VIII}$, and by inserting the value for b_{VIII} and $D = 2b_{VII}$ in Equation 3.4, b_{VI} can be determined. Since b_{VI} represents 2 protons, dividing b_{VI} by 2 gives the yield of molecule VI, see Equation 3.7.

$$Yield\ molecule\ VIII = \frac{c_{VIII}}{2} = \frac{E + D - 4}{2} \tag{3.6}$$

$$Yield\ molecule\ VI = \frac{b_{VI}}{2} = \frac{4 - D - 2c_{VIII}}{4} \tag{3.7}$$

3.2.2 Gas chromatography mass spectrometry/flame ionization detector (GC-MS/FID)

GC-MS/FID was done to qualitatively and semi quantitatively determine the products. One of the main products was molecule IV, which was not able to be identified by this method, due to its decomposition at elevated temperatures. Due to the low volatility of the products, the samples needed to be derivatized with *N*-Methyl-*N*-trimethylsilyl trifluoroacetamide (MSTFA) and Trimethylchlorosilane (TMCS). This was done by taking 0.1 g of the sample and solubilizing it in 10 ml pyridine, mixing it thoroughly. Afterwards, 50 µl of this solution is added to a gas chromatography vial, following adding 100 µl of MSTFA and 25 µl TMCS. The vial is heated to 80 °C under 30 minutes before analyzing it in GC-MS/FID. The gas chromatogram used helium as mobile phase and 7890A Agilent with a zebron ZB-5MSplus column (length=30, internal diameter=0.25 mm film thickness=0.25 µm) with flame ionization and mass quadripole detectors. The oven program used was 40 °C (1 min) →13 °C/min → 330 °C (10 min).

4

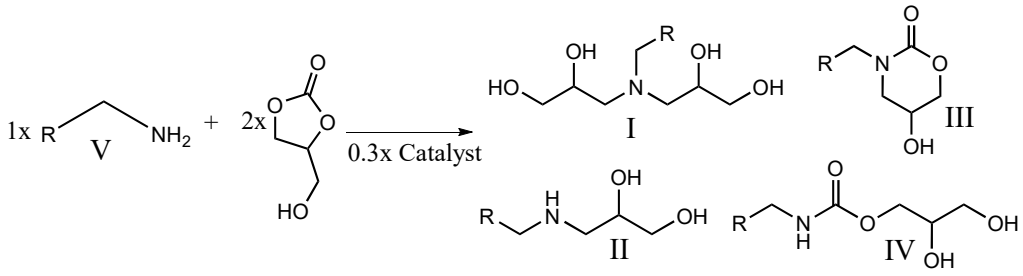
Results

The synthesize of nonionic surfactants from GC and primary FA were screened for different base catalysts (cat), with $Ca(OH)_2$ being further examined at different equivalents and temperatures. To assess the synthesis of tertiary alkylated amines, secondary FA were tested with $Ca(OH)_2$ and GC. To assess routes from readily available starting materials, the reaction between urea, glycerol, and FA was also investigated. The products were divided into the molecule categories I-VIII presented in chapter 3. However, structural isomers does occur for the final products, especially for III which also appears as a five membered ring. The GC-MS/FID results provided different isomers and polymers of those molecule categories and the raw data is provided in section A.1. Additionally, all of the GC/MS-FID results showed glycerol and polymerized versions of free glycerol, mostly diglycerol. The presented data in this section for GC-MS/FID are renormalized to exclude free glycerols to provide a yield based on the FA.

4.1 Investigating different catalyst for reaction between GC and primary FA

The reaction between GC and FA was investigated for three different catalyst with different alkalinity and with no catalyst. These reactions where screened for GC:FA:cat at 2:1:0.3 eq., for 6h at 210 °C. Based on ^{13}C NMR, signals for I-V was found for ZnO, MgO and $Ca(OH)_2$. Screenings without catalyst gave peaks for III and IV. The resulting ^{1}H NMR yields can be seen in Table 4.1. Without a catalyst, the yield of I and II was not detectable, however this system yielded 28 % of alkylated product due to III being formed. According to Table 4.1, adding a basic catalyst increased the yield of alkylated product significantly. For all of the reactions with catalyst, the yield of alkylated product was similar. However, increasing basicity from weakest for ZnO to strongest with $Ca(OH)_2$, resulted in more of the alkylated product being I and II and less of III.

Table 4.1: ^{1}H NMR yields obtained after reacting GC and FA at 210 °C for 6 h in the presence of $Ca(OH)_2$, MgO, ZnO, or without a catalyst (GC:FA:cat = 2:1:0.3).



Molecule	NMR yield %			
	$Ca(OH)_2$	MgO	ZnO	No cat
II+2I	46	30	29	–
III	19	28	31	28
IV	7	7	7	17
Total Alkylated	65	58	60	28

GC-MS/FID was done on screenings for GC:FA:cat at 2:1:0.3 eq., for ZnO and MgO at 210 °C and $Ca(OH)_2$ at 220 °C for 6 h. According to GC-MS/FID Table 4.2, $Ca(OH)_2$, MgO and ZnO yielded molecules I-V and ZnO also gave trace amounts of 4-Dodecyl-2,5-dimethanol-morpholine (Morpholine). The structure for the morpholine derivative can be seen in Figure A.1. None of the catalyst gave full conversion, with $Ca(OH)_2$ showing the highest conversion and ZnO the lowest. The yielded morpholine derivative, is a tertiary alkylated product, which in the reaction is formed via I, where I is first formed, following dehydration [27]. Based on these results, the yield of I is highest for $Ca(OH)_2$ and lowest for ZnO. However, ZnO gave the second highest yield of tertiary alkylated products.

Table 4.2: GC-MS/FID results for $Ca(OH)_2$, MgO and ZnO. The $Ca(OH)_2$ result is from reacting for 6h at 220 °C, (GC:FA:cat = 2:1:0.3) , followed by catalyst removal via precipitation in IPA and filtration. The MgO and ZnO results are from reaction at 210 °C for 6 h, (GC:FA:cat = 2:1:0.3). Raw data can be seen in Table A.3.

Molecule	Area %		
	$Ca(OH)_2$	MgO	ZnO
I	20	7	4
II	24	14	9
III	43	60	57
V	14	19	19
Morpholine	–	–	5
Unknown	–	–	6
Total Alkylated	87	81	75

4.2 Reaction between GC and primary FA at different temperatures

The reaction between primary FA, GC and $Ca(OH)_2$ was further investigated at different temperatures at equivalents for GC:FA:cat at 2:1:0.3. Initially, the reaction was tested for 4 h at temperatures 150-190 °C each, see Figure 4.1. At 150 °C and above, the peak for I, II and V started to grow, however, with the model for calculating the NMR yield, these areas were too small to determine the yield. This was true for all temperatures below 190 °C. At 190 °C, an increase in magnitude for the peaks corresponding to I and II led to a significant increase in the alkylated product. The yield of cyclic carbamates (III) slightly increased with increasing temperature. Additionally, without catalyst, at 150 °C after 6 h synthesis GC:FA 2:1, 12 % of III was yielded, see Table A.8.

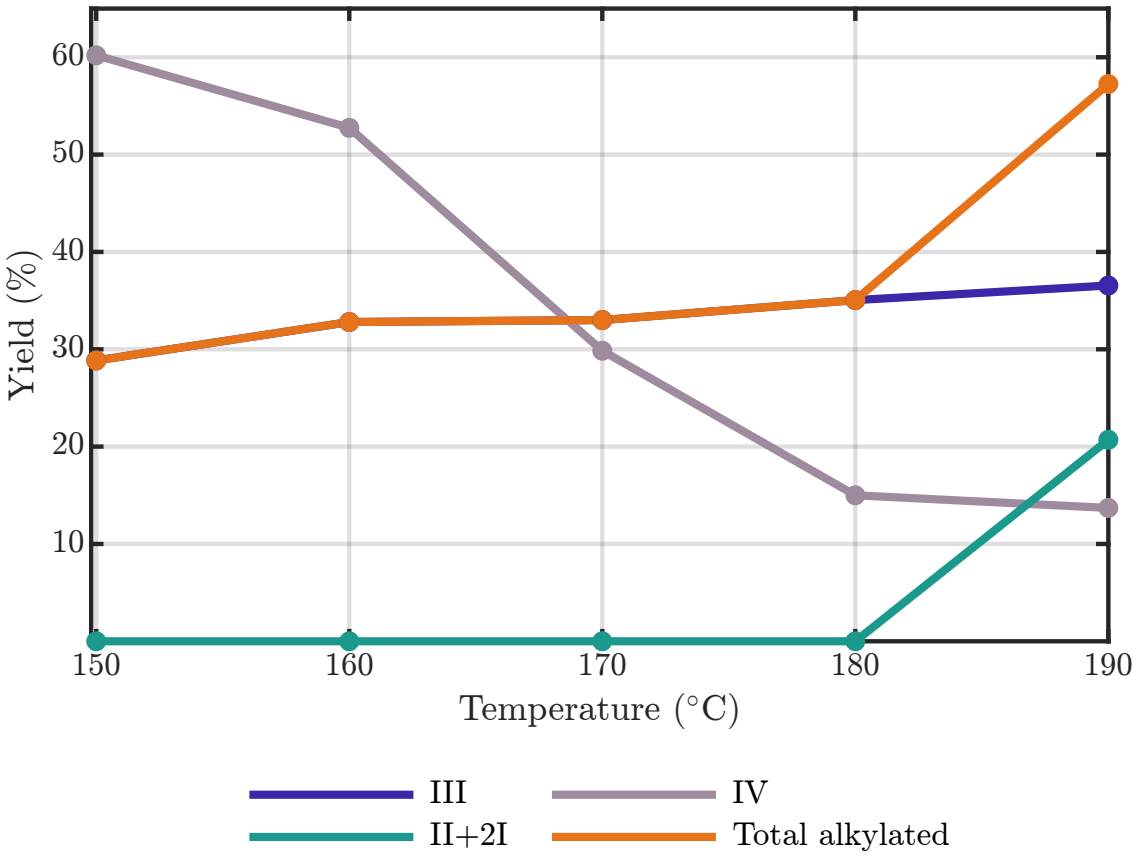
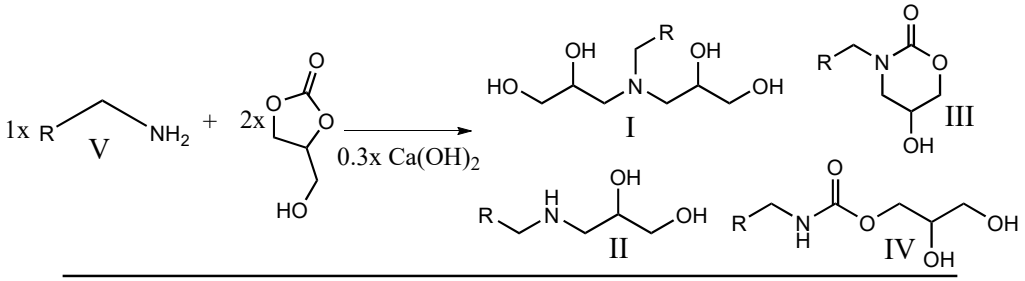


Figure 4.1: ^{1}H NMR yields plotted from reacting FA, GC and $Ca(OH)_2$ for 4 h at temperatures 150-190 °C, GC:FA:cat (2:1:0.3). See Table A.6 for raw data.

Due to the fact that the yield of alkylated product had its peak at the highest temperature, an additional temperature screening was done for 190, 200, 210, 220 and 230 °C, for 6 h. According to Table 4.3, 210 °C gave the highest amount of alkylated product, while both 190 and 230 °C gave the lowest yield.

Table 4.3: ^{1}H NMR yields after reacting GC with primary FA at 190–230 °C for 6 h using $Ca(OH)_2$ (GC:FA:cat = 2:1:0.3).



Molecule	NMR yield %				
	190 °C	200 °C	210 °C	220 °C	230 °C
II+2I	22	24	46	49	35
III	31	37	19	15	13
IV	11	12	7	6	7
Total Alkylated	53	61	65	64	48

According to Figure 4.2, the yield of alkylated product is similar for 200, 210 and 220 °C, however their composition is different. At 200 °C, the majority of the alkylated product is III, while at 210 and 220 °C, the majority are I and II. With 39, 71 and 77 % of the alkylated product being I and II for 200, 210 and 220 °C respectively. Additionally as can be seen in Figure 4.2, the datapoints for 230°C shows different behaviour than the other temperatures. These results suggests that above 220 °C, the yield of I and II is significantly decreased, due to other competing reactions starting to take place at 230 °C. The highest NMR yield of III, could be found at 190 °C while for I and II, 220 °C gave the highest yield. For this temperature screening, V was identified in ^{13}C NMR.

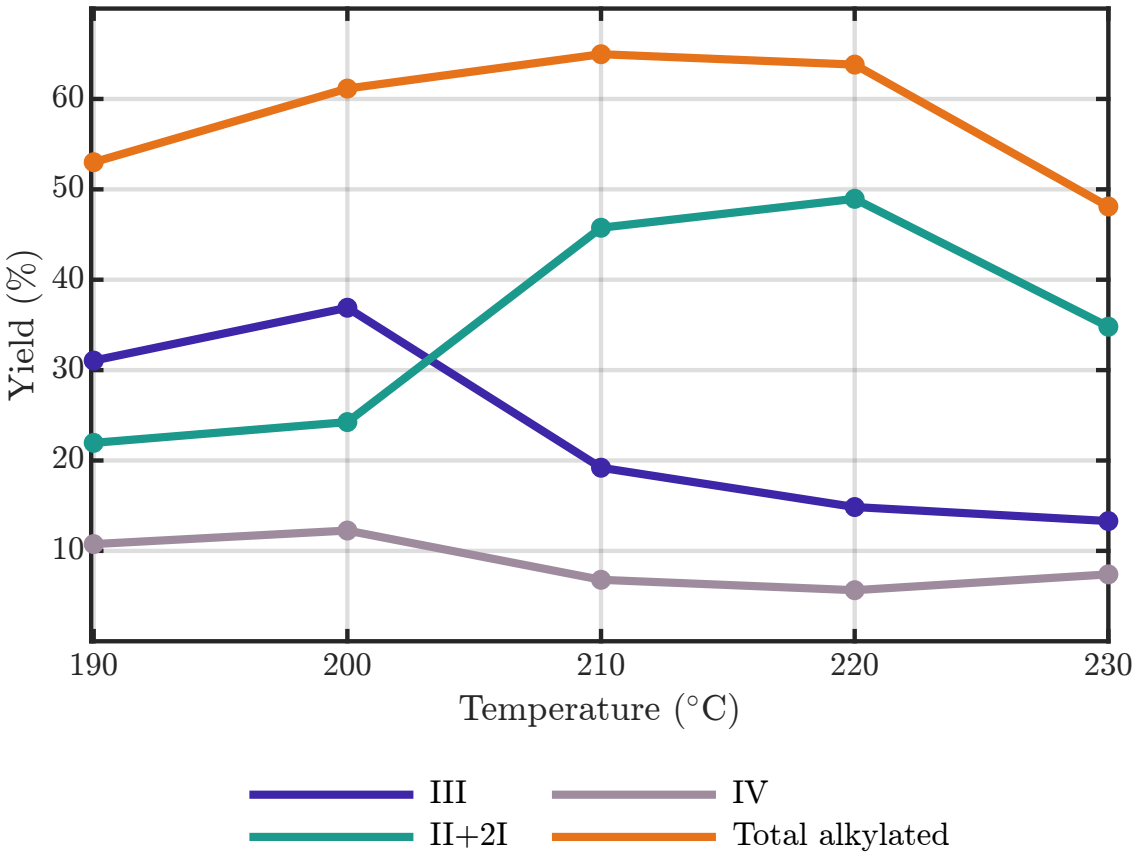
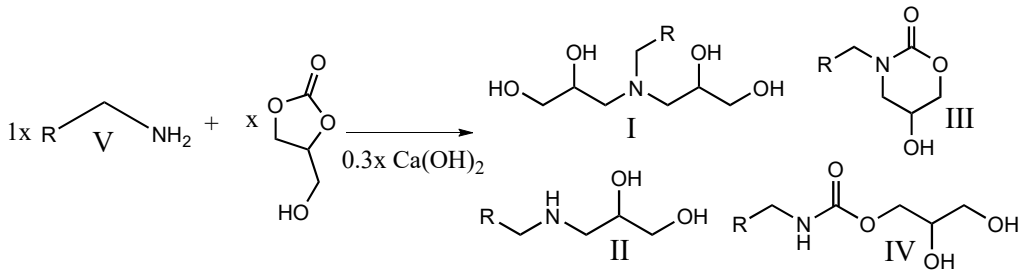


Figure 4.2: Plot of Table 4.3. This plot shows the product outcome and behavior depending on temperatures between 190-230 °C.

4.3 Reaction between GC and primary FA with $Ca(OH)_2$ at different amounts of GC.

The reaction between GC, primary FA and $Ca(OH)_2$ was investigated for FA:cat (1:0.3) and different equivalents of GC, (1-6 eq.), at 210 °C for 6 h. The NMR yield is summarized in Table 4.4. Based on ^{1}H NMR, 2 and 4 eq. of GC yielded the most amount of alkylated product. For 2 eq. of GC, the peak for FA is detectable in ^{13}C NMR, however, in ^{1}H NMR it is overlapping with I and II, this leads to the amount of FA left in the product not being quantifiable, see chapter 3. For 4 and 6 eq., the peak for FA in ^{13}C NMR is not detectable and for 1 eq. of GC, I and II is not detectable in ^{13}C NMR, leading to the yield for FA being able to be determined in ^{1}H NMR.

Table 4.4: ^{1}H NMR yields after 6 h reaction at 210 °C using varying equivalents of GC (1–6 eq), FA (1 eq), and $Ca(OH)_2$ (0.3 eq).



Molecule	NMR yield %			
	1 GC	2 GC	4 GC	6 GC
II+2I	–	46	31	17
III	14	19	35	33
IV	75	7	19	17
V	8	unknown	–	–
Total Alkylated	14	65	66	50

According to Figure 4.3, at 1 GC eq. the yield of I and II could not be detected, while a substantial amount of the product was IV and less amount of III was yielded. This made 1 GC eq. have the lowest yield of alkylated product. At 2 GC eq. the highest amount of I and II could be detected while at 4, the largest amount of III could be detected. At GC eq. over 4, the peak for I and II notably diminishes. At 1, 2, 4 and 6 GC eq., 0, 71, 47 and 34 % of the alkylated product was I and II.

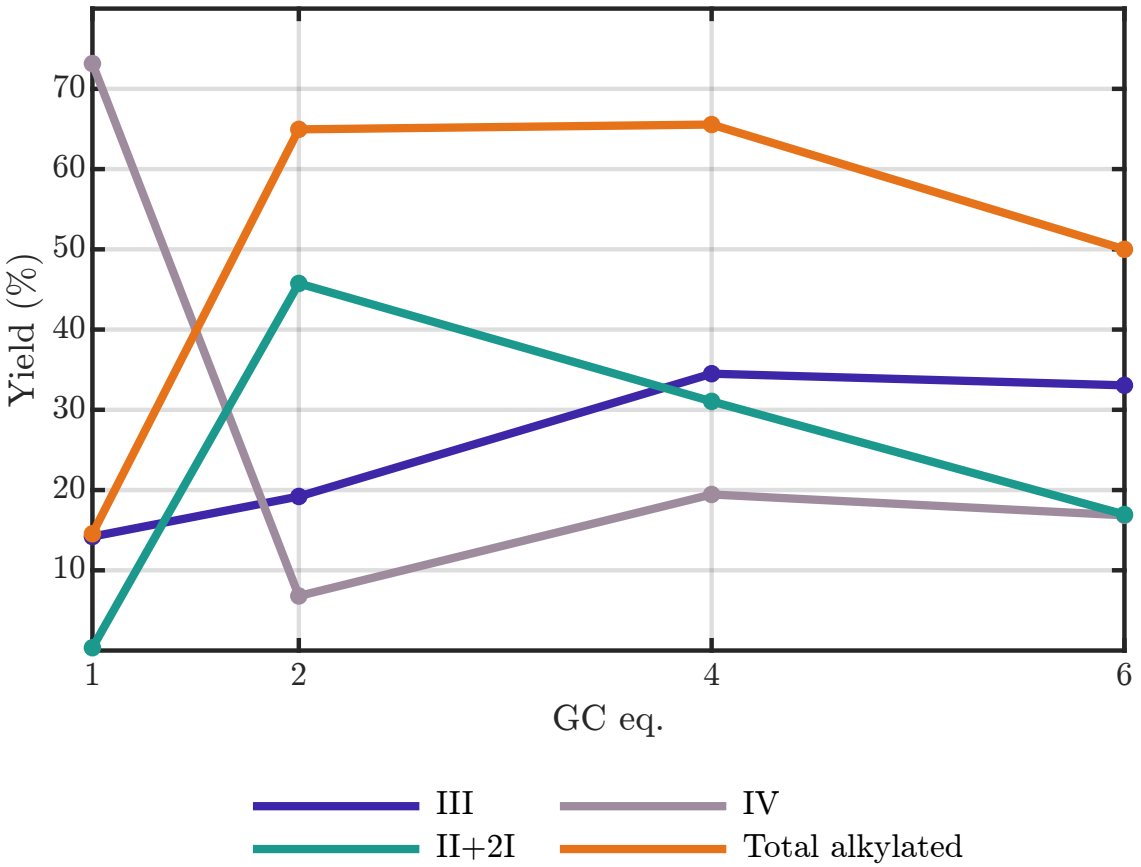


Figure 4.3: This is a plot of Table 4.4. ^{1}H NMR yields after 6 h reaction at 210 °C using varying equivalents of GC (1–6 eq.), FA (1 eq.), and $Ca(OH)_2$ (0.3 eq.).

According to a GC-MS/FID taken for 4 eq. of GC in Table 4.5, 100 % of the product was alkylated and no V was detected. Since GC-MS/FID does not detect IV and the NMR yield detected 19 % , it can be concluded that the yield of alkylated product for 4 GC eq. is high, however there is not 100 % conversion. The detected area % of II was only 7 area % and no II was detected, however the GC-MS/FID results done on the hydrolyzed product showed trace amounts of I.

Table 4.5: GC-MS/FID results after synthesis for 6h at 210 °C, for FA (1 eq.), GC (4 eq.) and $Ca(OH)_2$ (0.3 eq.). Raw data can be seen in Table A.5.

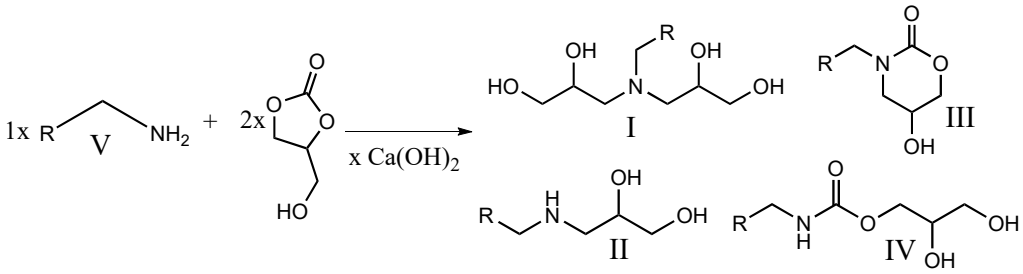
Molecule	**Area %**
II	7
III	93
Total Alkylated	100

4.4 Evaluating catalyst concentration

The reaction between GC, primary FA and $Ca(OH)_2$ was investigated for FA:GC (1:2) and different equivalents of catalyst, (0-0.3 eq.), at 210 °C for 6 h. The NMR

yield is summarized in Table 4.6. According to Table 4.6, the yield of alkylated FA was the highest for 0.2 and 0.3 equivalents. In comparison to no catalyst, adding 0.15 eq. of catalyst increases the alkylated product yield with 200 %. The yield of IV is the highest without catalyst and the lowest for 0.3 eq. For 0.3, 0.25, 0.2 and 0.15, the percentage of alkylated product that is I and II is 71, 60, 64 and 55 %.

Table 4.6: ^{1}H NMR yields after 6 h reaction at 210 °C using varying equivalents of $Ca(OH)_2$ (0-0.3 eq.), FA (1 eq.), and GC (2 eq.).



	NMR yield %				
Molecule	0.3 cat	0.25 cat	0.2 cat	0.15 cat	No cat
II+2I	46	38	47	33	–
III	19	25	27	27	28
IV	7	10	11	11	17
Total Alkylated	65	63	74	60	28

4.5 Hydrolysis of carbamates

After synthesis, the hydrolysis procedure described by Lattuada et. al (2022) [8] was tested. The intent was to hydrolyze III to II and IV to V. The product from section 4.2 where GC:FA:$Ca(OH)_2$ (2:1:0.3) was reacted for 6h at 210 °C, was hydrolyzed using 5 eq. of NaOH per carbamate (III and IV), for 3 h at 80 °C. According ^{1}H NMR, III went from 19 % yield before hydrolysis to 6 % yield after hydrolysis and for IV, 7 % yield before and 6 % after. The product after hydrolysis was analyzed with GC-MS/FID and the final product composition can be seen in Table 4.7. Based on the GC-MS/FID results, 69 % of the product after hydrolysis is either I or II and 5 % III is still left in the product.

Table 4.7: GC-MS/FID results after doing base hydrolysis on the sample from the temperature screening at 210 °C from section 4.2. Base hydrolysis was done with 5 eq. of NaOH per carbamate (III and IV) in EtOH/water, for 3 h at 80 °C. Detailed information can be seen in Table A.2

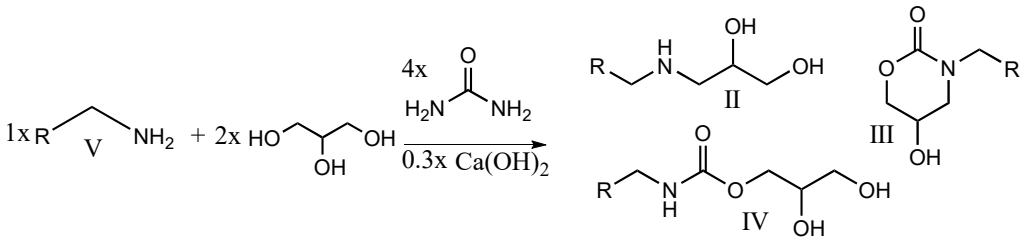
Molecule	Area %
I	9
II	60
III	5
V	14
Unknown	8
Didodecylamine	4

The same procedure was done for the sample with 4 eq. of GC. According to ^{1}H NMR, III went from 35 % yield before hydrolysis to 5 % yield after hydrolysis and for IV, 19 % yield before and 10 % after. The product after hydrolysis was analyzed with GC-MS/FID and the final product composition can be seen in Table A.1. According to these results, 25 % of of cyclic carbamates (III) were still left in the sample, suggesting that the procedure needs more time to hydrolyze when increasing the amount of carbamates in the product.

4.6 Reaction between glycerol, urea and primary FA

FA, glycerol, urea and $Ca(OH)_2$ (1:2:4:0.3 eq.) were reacted at the temperatures between 140 °C-190 °C, see detailed conditions in section A.4. The renormalized results from GC-MS/FID with respect to urea (WRT urea) and with respect to fatty amine (WRT FA) can be found in Table 4.8. WRT urea and WRT FA reports the relative distribution of products formed via reactions involving urea or FA, respectively. These results are used to give an understanding of the yield with respect to urea or FA. Based on these results, with respect to urea and FA, 59 % and 50 % of the product were alkylated. WRT FA, had 28 % of FA left in the product. WRT FA, showed that 22 % of the product is either unknown or other products, which are most likely the result of FA and urea reacting. The resulting product for WRT urea, consisted of considerable amounts of unalkylated products such as imidazole and serinol carbamate. No traces of I could be found.

Table 4.8: GC-MS/FID results after reacting urea (4 eq.), glycerol (2 eq.) and FA (1 eq.). Raw data can be seen in Table A.4.



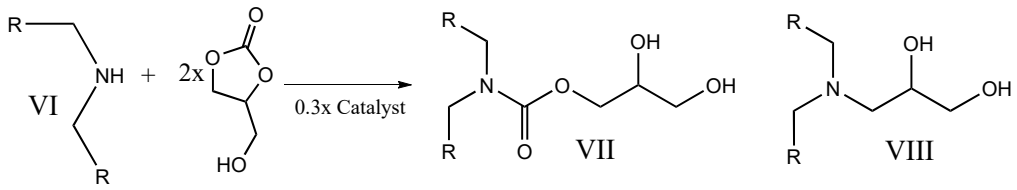
Molecule	WRT urea	WRT FA
II	3	2
III	46	39
V	–	28
N-alkylated imidazole	10	9
Imidazole	3	–
Serinol carbamate	10	–
Other	22	17
Unknown	6	5
Total alkylated	59	50

II-V was detected in ^{13}C and ^{1}H NMR. The resulting ^{1}H NMR yields are summarized in Table A.7. The yield for III, IV and V are based on integration of ^{1}H NMR peaks and the summarized resulting yields are more than 100 %, suggesting that there is an overestimation. This overestimation is likely to be from the peak for FA, where most likely II also is shown in small amounts. However, especially for IV, there is no sign of overlapping with other products, where the NMR yield was estimated to be 33 %. This was determined with gHSQCAD. In ^{13}C NMR, the signal for FA was strong, suggesting that considerable amount of unreacted FA is left in the product. The peak for *N*-alkylated imidizaole, imidazole and serinol carbamate are slightly shifted downfield in proton NMR, making it not possible to quantify with ^{1}H NMR since it overlaps with the glycerol peaks.

4.7 Reaction between GC and secondary FA

Secondary FA and GC was reacted with $Ca(OH)_2$ (1:2:0.3 eq.) at 160 °C for 3 h and 190 °C for 2h. Already after 3 h at 160 °C, the peak for VIII started to appear. After 3 h at 160 °C and 2 h at 190 °C the yield of VI, VII and VIII was determined in Table 4.9.

Table 4.9: ^{1}H NMR yields after synthesis with GC (2 eq.), secondary FA (1 eq) and $Ca(OH)_2$ (0.3 eq.).



Molecule	Yield %
VII	33
VIII	54
VI	13
Total Alkylated	54

5
Discussion

Based on the reaction mechanism proposed in section 1.1, the reaction between GC and FA can be seen in Figure 5.1. Reaction step 1-5, have its own reaction rates which are affected by both kinetics and thermodynamics. According to [6], the suggested reaction mechanism in section 1.1 shows that the equilibrium is between a serinol and an *N*-(2,3-dihydroxypropyl)urea. However, it is also mentioned that serinol will convert to *N*-(2,3-dihydroxypropyl)urea, if ammonia is not removed during the reaction. Since ammonia is yielded when forming serinol carbamates, this would suggest that step 4 is also an equilibrium step. Based on both NMR and GC-MS/FID, one of the main products in this thesis is glycerol. Since step 4 is an equilibrium reaction, even though a lot of glycerol is yielded, the equilibrium still seems to be strongly shifted towards III. This would suggest that product III is a thermodynamically stable product.

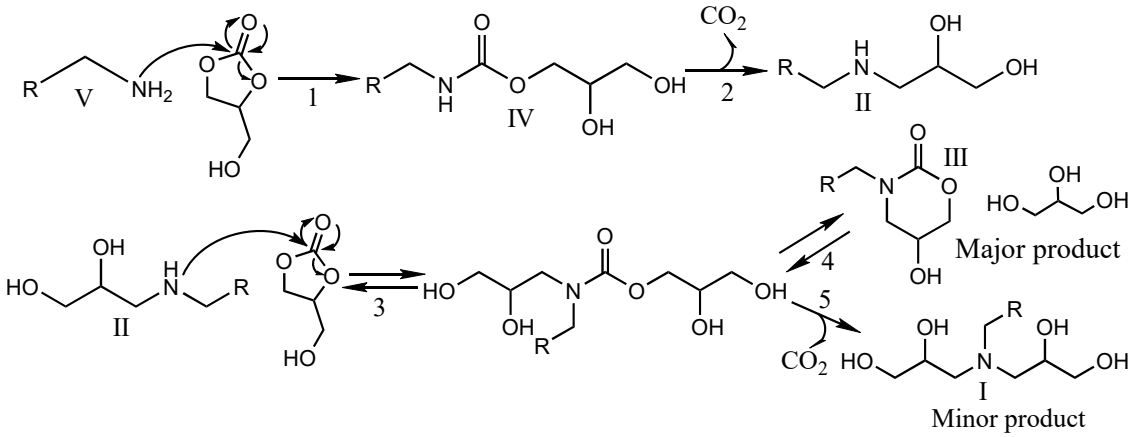


Figure 5.1: Proposed mechanism when reacting GC and FA with $Ca(OH)_2$, MgO or ZnO as catalyst.

Furthermore, adding a basic catalyst in comparison to no catalyst increase the yield of alkylated amines, and decreased the yield of carbamates. The strength and amount of basic sites goes from strongest to weakest for $Ca(OH)_2$, MgO and ZnO and by increasing the strength and amount of basic sites for the catalyst, the yield of alkylated product is slightly increased. However, the yield of I and II is significantly increased for $Ca(OH)_2$ in comparison to MgO and ZnO. For MgO and ZnO, the yield of III is higher than for $Ca(OH)_2$.

This could suggest that adding a basic catalyst will introduce alternative reaction

pathways with lower activation energy for one or more steps for the reaction mechanism of alkylated amines, suggested in Figure 5.1, such as step 2-5. This results in low yield of IV, but increased yield of I-III. This could especially be seen for MgO and ZnO, where less IV was left in the product, high amount of III and some I and II was yielded in comparision to no catalyst, where high amount of IV was left and similar amount of III was produced.

Both III and I needs 2 GC to be formed, which makes them competing reactions. As mentioned previously, III is especially thermodynamically stable, which is assumed to be the contributing reason why the reaction is heavily shifted towards III and not I. For $Ca(OH)_2$, the yields of I and II increased and both carbamate molecules (III and IV) were lower compared to no catalyst and other screened catalyst systems. In particular, the yield of I was higher. This could suggest that using an alkaline catalyst with strong basic sites could introduce alternative side reactions, such as decomposition of GC into glycidol, suggested in section 1.1, which will react with the FA. This reaction path, will compass the production of both III and IV leading to higher yields of I and II.

By also investigating the reaction between secondary FA and GC, one could investigate the synthesize of tertiary alkylated amines (I and VIII). This trial eliminated the competing reactions between III and I. These results suggested that at lower temperatures and shorter reaction times, the yield of tertiary alkylated amines (VIII) was substantial. This indicates that, in reactions between primary FA and GC, the low yield of tertiary alkylated amines (I) is not necessarily due to this pathway being unfavorable. However, compared to cyclic carbamates (III), the reaction rate is much lower $r_4 >> r_5$.

Additionally, the yield of I and II seems to be more sensitive to lower amounts of GC in comparison to III, since even at 1 eq. of GC, there was some III formed whilst I and II was undetectable. This would also suggest that under these reaction conditions, step 4 is highly favorable. Additionally, by increasing the amount of GC from 2 to 4 eq., the yield of III increased, whilst both I and II decreased. II will most likely be consumed to produce molecules with 2 glycerol units. However, by increasing the amount of GC, no product I is yielded whilst a significantly higher yield of III is obtained, which would suggest that $r_4 >> r_5$. This difference in reaction rates, when increasing the amount of GC could suggest that the reaction order for step 4, is higher than step 5.

The synthesis of alkylated products starts at 150 °C, with and without catalyst in the form of III. The yield of alkylated product increases considerably above 180 °C, due to the substantial increase of I and II above 180 °C. The maximum yield is found at 210-220 °C. Above 200 °C, the yield of III decrease whilst the yield of I and II keep increasing. The decrease in carbamates (IV and III) at elevated temperatures could be due to the increase in the irreversible decomposition reaction, step 2 and 5, suggested in Figure 5.1 or/and the increase in the GC decomposition to glycidol. This would suggest that these irreversible reactions are limited by their activation energy, which with increasing temperature will result in increased reaction rates.

GC is less readily available in comparision to glycerol and urea so a onepot reaction starting with urea, GC, FA and $Ca(OH)_2$ was also tested. Based on the GC-MS/FID results, around 59 % of the product with respect to urea, made alkylated products. However, 50 % of the FA, became an alkylated product while around 28 % was the unreacted FA. Of that alkylated product, small amounts of II was found and no I. In comparison to the GC-MS/FID results for 220°C with GC and FA, there was a larger variety of products and less yield of alkylated products. Which would suggest that using urea and glycerol in comparison to GC, results in a less selective reaction towards alkylated products (I, II and III).

Additionally, as mentioned, urea was in greater excess than the FA and glycerol. However, larger amount of the urea became an alkylated product in comparison to the FA. This could suggest that large amount of urea was lost during the reaction due to the decomposition reaction to ammonia, which evaporated instead of staying in the reaction vessel. This could explain why significant amount of unreacted FA was left and why more of the urea yielded an alkylated product than the FA, even though urea was in 4 times excess. By changing to a closed system, it is possible that the same reaction conditions could result in higher conversion.

The considerable amount of different unalkylated products and unreacted FA suggests that there are other competing reactions to the alkylation. For this reaction, another way to reach full conversion or similar conversions to GC, would be by increasing the equivalent of glycerol and urea. However, this will most likely also increase the amount of unalkylated product as well. Additionally, according to NMR, there is a lot of IV left in the product. From doing the GC equivalents screenings, increasing the amount of GC between 1 eq. to 2 or 4 increases the amount of alkylated product and decreases amount of IV. It is possible that due to decomposition of urea and other reactions consuming urea and glycerol, the glycerol and urea equivalents in relation to FA could be shifted towards a 1:1:1 ratio. By increasing the amount of urea and glycerol, it is possible that less of IV could be produced, full conversion of the FA could be reached and more of III could be formed. However, this will most likely also increase the yield of unalkylated products.

Additionally, increasing the amount of urea and glycerol will most likely not increase yield of I or II. II will further react and I will be competing with other reactions, resulting in low yields.

6
Conclusion

Based on these results, it is possible to yield *N*-alkylated FAs by reacting GC or glycerol and urea with a FA at temperatures at and above 150 °C with or without catalyst. The final product contains a mix of FA, 2,3-dihydroxypropyl *N*-alkylcarbamate (IV), *N*-alkyl serinol carbamate (III), 2,3-dihydroxypropyl amines (II), Bis-2,3-dihydroxypropyl amines (I) and glycerol. By adding a basic catalyst such as $Ca(OH)_2$, MgO or ZnO, the yield of alkylated product can be improved. In the reactions with primary FAs, the reaction exhibited high selectivity towards III, however, by using a catalyst with stronger basic properties, such as $Ca(OH)_2$, larger amounts of the alkylated products are II and I. Elevating the temperatures to between 200-220 °C, adding 2-4 GC eq. and 0.2 or 0.3 eq. of $Ca(OH)_2$ gave the highest yield of alkylated product.

It is possible to increase the yield of I by hydrolyzing III after the initial reaction. By changing GC to urea and glycerol, the selectivity towards alkylated products decreased. When using urea and glycerol, the majority of the alkylated product was III, while trace amounts of II were found. For both reactions with GC and glycerol with urea, the yield of products consuming 2 GC units seems to be heavily shifted towards III and less towards I. By increasing the amount of competing reactions by changing GC to glycerol and urea, the yield of I and II becomes negligible.

6.1 Future outlook

For future studies, it should be evaluated if polyglycerol carbonates and FAs derived from coconut or tallow could be used for this chemistry. Furthermore, analyzing the surface activity of the final polyglycerol surfactants is necessary for evaluating their functionality. To maximize the yield of alkylated product and provide a reaction procedure with as high atom economy as possible, it should be investigated if glycerol and CO_2 could be removed during the reaction and be reused to produce more GC. Additionally, by removing glycerol during the reaction, it could possible shift the equilibrium reaction towards product III, resulting in increased conversion.

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A

Appendix 1

A.1 GC-MS raw data

This section summarizes all of the GC-MS/FID results with all of the components found in the analysis, before renormalization. The data presented in chapter 4 is based on this data, where the molecules are put into the categories I-VIII, other and more. Molecules identified by GC/MS-FID are listed in Figure A.1 and are referred to accordingly in tables in this section.

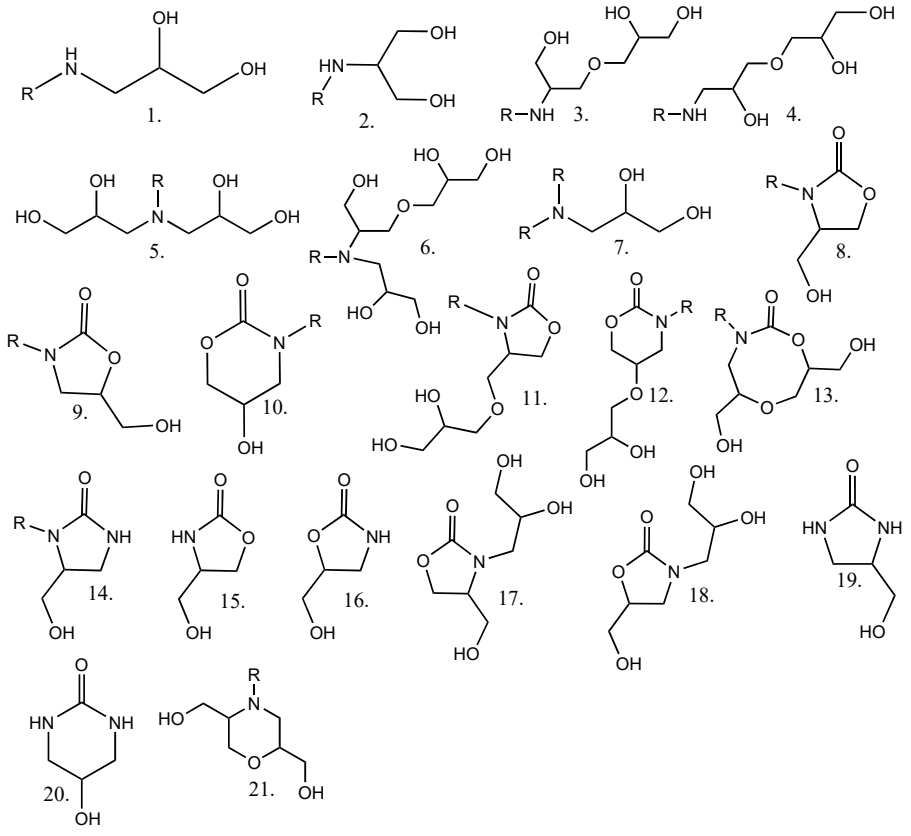


Figure A.1: These molecules will be refereed to in GC-MS/FID table results. These results show the different isomers in the product.

Table A.1: This is the GC-MS/FID results for 4 eq. of GC after base hydrolysis, seen in section 4.5.

Molecule	**Area %**
Compound 1	36.915
Compound 2	19.231
Compound 4	7.655
Compound 5	2.687
Compound 6	3.497
Compound 8	2.489
Compound 9	22.139
Dodecylamine	1.748
Unknown	3.639

Table A.2: This is the GC-MS/FID results for 210 °C after base hydrolysis, seen in Table 4.7.

Molecule	**Area %**
Compound 1	30.717
Compound 2	8.471
Compound 3	1.585
Compound 4	2.888
Compound 5	7.784
Compound 6	1.610
Compound 9	5.119
Didodecylamine	3.699
Compound 10 w *N*-acetamide	2.963
Compound 1 w *N*-acetamide	9.126
2,3-dihydroxypropyl-didodecylamine	3.699
Dodecylamine	15.374
Unknown	9.732

Table A.3: This is the GC-MS/FID results for $Ca(OH)_2$, MgO and ZnO, seen in Table 4.2. The $Ca(OH)_2$ result is from 220 °C after the catalyst has been removed with IPA and the result for MgO and ZnO is from synthesis at 210 °C.

Molecules	Area %		
	$Ca(OH)_2$	MgO	ZnO
Glycerol	48.2711	39.175	45.194
Dodecylamine	4.30898	9.009	8.316
Diglycerine	20.4134	13.664	10.588
Compound 1	7.54335	6.5	3.928
Compound 9	7.86152	–	4.118
Compound 8 and 10	5.46366	27.1	21.278
Compound 5	6.14004	3.253	1.897
Compound 13	–	1.299	–
Compound 21	–	–	1.968
Unknown	–	–	2.715

Table A.4: This is the GC-MS/FID results for glycerol, urea and FA reaction with $Ca(OH)_2$ as catalyst, seen in Table 4.8.

Molecule	Area %
Glycerol	13.705
Decylamine	21.308
Diglycerine	1.538
Compound 1	1.602
Compound 10	29.196
Compound 14	6.537
Compund 15	0.76
Compound 16	1.366
Compound 17	2.108
Compound 18	2.004
Compound 19	1.247
Compound 20	0.704
3-Amino-1,2-propanediol	1.301
Carbamate	2.238
Decane isocyanate	3.552
N,N'-di(nonyl)methanediimine	2.449
N,N'-dinonylurea	4.679
Unknown	3.706

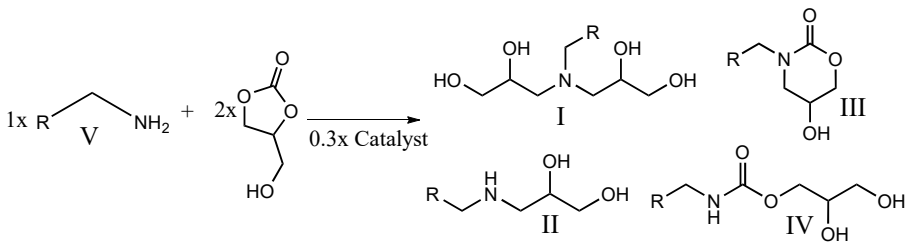
Table A.5: This is the GC-MS/FID results for 4 eq. of GC, seen in Table 4.5.

Molecule	Area %
Glycerol	24.073
Cyclic glycerol	5.351
Diglycerol	26.009
Triglycerol	9.127
Compound 1	1.526
Compound 2	1.114
Compound 8	15.011
Compound 10	11.197
Compound 11	2.685
Compound 13	3.906

A.2 NMR yield data

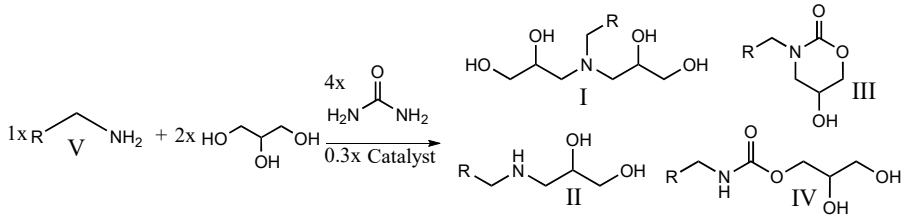
This section shows the NMR yields for data in chapter 4 that was not presented in table form.

Table A.6: This is the ^{1}H NMR yield results for the synthesis at different temperatures (150-190 °C) for eq. 1:2:0.3 between FA, GC and $Ca(OH)_2$ after 4 h synthesis seen in Figure 4.1.



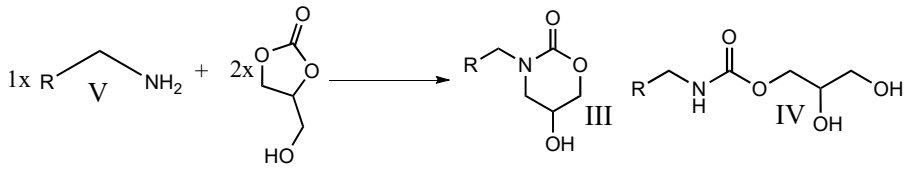
	NMR yield %				
Molecules	150 °C	160 °C	170 °C	180 °C	190 °C
II+2I	0	0	0	0	21
III	29	33	33	35	37
IV	60	53	30	15	14
Total alkylated	29	33	33	35	57

Table A.7: This is the ^{1}H NMR yield results after reacting glycerol, urea and FA with $Ca(OH)_2$ as catalyst seen in section 4.6.



Molecule	Yield %
IV	33
III	58
V	14

Table A.8: This is the ^{1}H NMR yield results after reacting GC and FA at 150 °C for 6h, seen in section 4.2.



Molecule	Yield %
III	76
IV	12

A.3 NMR spectroscopy data

This section summarizes the chemical shifts for the main molecules of interest, molecule I-VIII. Additionally, some NMR spectras are presented to show a typical NMR spectra for the reactions and the ones with peaks that are outliers. All of the samples where prepared with 50:50 vol% Chloroform D and Methanol-D.

A.3.1 NMR spectroscopy chemical shift data

2,3-dihydroxypropyl *N*-decylcarbamate (IV): ^{1}H NMR (400 MHz, 50: 50 vol% $CDCL_3$:CD_3OD): δ (4.0598,COO-(CH2)-CHOH, 2H, m), (3.8394-3.7549, CH2-(CH)OH-CHOH, 1H, m), (3.5966, (CH2)OH-CHOH, 2H,d, J=unclear), (3.0759, N-(CH2)-R, 2H, t, J=7.02 Hz), (1.3507-1.1881, CH3-(CH2)n-CH2, 14H,m), (0.8554, CH3, 3H, t, J=6.88 Hz)

2,3-dihydroxypropyl *N*-decylcarbamate (IV):^{13}C NMR (400 MHz, 50:50 vol% $CDCL_3$:CD_3OD): δ (158.2635-157.8333 NH-(C)OO-CH2), (70.8999, 1C), (66.2422,

1C), (63.8933, 1C), (41.6078-41.3164, N-(CH2)-CH2, 1C), (32.41377, 1C), (30.6416-29.5903, 5 C), (27.3287, 1C), (23.1742, 1C), (14.2998 ,CH3, 1C).

***N*-decyl serinol carbamate (III)**: ^{1}H NMR (400 MHz, 50: 50 vol% $CDCL_3$:CD_3OD): δ (Peaks between 4.7-3.33 are the remaining peaks from the cyclic carbamate N-(CH2-CHOH-CH2)-O), (3.2150, R-(CH2)-N, 2H, t, J=7.20 Hz), (1.5819-1.4978, R-(CH2)-CH2N, 2H, m), (1.4924-1.3863,R-(CH2)-CH2CH2N, 2H,m),(1.3507-1.1881, CH3-(CH2)n-CH2, 12H, m), (0.8554, CH3, 3H, t, J=6.92 Hz)

***N*-decyl serinol carbamate (III)**: ^{13}C NMR (400 MHz, 50:50 vol% $CDCL_3$:CD_3OD): δ (159.6521, R2N-(C)OO-CH2, 1C), (74.6173, CH2-(C)HOH-CH2, 1C),(63.0508, COO-(C)H2-COH, 1C), (46.4010, N-(C)H2-CHOH, 1C), (44.5481, R-(C)H2-N, 1C), (32.4818, R-(C)H2-CH2-N, 1C), (30.4793-29.7191, R-(C)H2-(C)H2-CH2), 2C), (28.1115-27.1038, 4C), (23.2235, 1C), (14.3238 , CH3, 1C)

2,3-dihydroxypropyl decylamines (II): ^{1}H NMR (400 MHz, 50: 50 vol% $CDCL_3$:CD_3OD): δ (3.7841-3.6633, N-CH2-(CH)OH-CHOH, 1H, m), (3.5215, OH(CH2)-CHOH, 2H, d, J=unclear), (2.7046-2.3866,R-(CH2)-N-(CH2)-Gly, 4H), (1.5557-1.3785, R-(CH2)-CH2, 2H, m), (1.3524-1.1575, CH3-(CH2)n-CH2, 14H, m), (0.8645, CH3, 3H, t, J=6.88 Hz)

2,3-dihydroxypropyl decylamines (II):^{13}C NMR (400 MHz, 50:50 vol% $CDCL_3$:CD_3OD): δ (70.2254-69.8021, CH2-(CH)OH-CH2, 1C), (65.7328-65.2821, HO-(C)H2-, 1C), (52.8058, Glyc-(C)H2-NH-R, 1C), (50.3552, Glyc-CH2-NH-(C)H2-R, 1C), (32.5274, 1C), (30.2471, 3C), (29.9319, 1C), (28.0499, 1C), (27.2719, 1C), (23.2235, 1C), (14.3238, CH3, 1C)

Bis-2,3-dihydroxypropyl decylamines (I): ^{1}H1H NMR (400 MHz, 50: 50 vol% $CDCL_3$:CD_3OD):δ (3.7911-3.3.6689, N-2xCH2-(CH)OH-CHOH, 2H, m), (3.5215, 2xOH(CH2)-CHOH, 4H, d, J=unclear), (2.7046-2.3866,R-(CH2)-N-2x(CH2)-Gly, 6H), (1.5358-1.3755, R-(CH2)-CH2, 2H, m), (1.3281-1.1816, CH3-(CH2)n-CH2, 14H, m), (0.8645, CH3, 3H, t, J=6.88 Hz)

Bis-2,3-dihydroxypropyl decylamines (I): ^{13}C NMR (400 MHz, 50:50 vol% $CDCL_3$:CD_3OD): δ (70.2254-69.8021, 2xCH2-(C)OH-CH2), 2C), (65.7328-65.2821, 2xHO-(C)H2, 2C), (58.9590-58.2773, 2xGlyc-(CH2)-NH-R, 2C), (56.4339, NH-(C)H2-R, 1C), (32.5274, 1C), (30.2471, 3C), (29.9319, 1C), (28.0499, 1C), (27.2719, 1C), (23.2235, 1C), (14.3238, CH3, 1C)

2,3-dihydroxypropyl *N*-dihexylcarbamate (VII): ^{1}H NMR (400 MHz, 50:50 vol% $CDCL_3$:CD_3OD): δ(4.0582, COO-(CH2)CHOH, 2H, m), (3.540, (CH2)OH, 2H, d, J=unclear), (3.208, N-2x(CH2)-CH2, 4H, t, J=7.54 Hz), (1.5649-1.4754, 2xCH2, 4H, m), (1.3598-1.1882, 2xCH2-(CH2)3-CH2, 12H, m), (0.8757, 2xCH3, H, t, J=6.86 Hz)

2,3-dihydroxypropyl *N*-dihexylcarbamate (VII):^{13}C NMR (400 MHz, 50:50 vol% $CDCL_3$:CD_3OD): δ (157.5294, NH-(C)OO-CH2), (70.9165, CH2-(CH)OH-CHOH, 1C), (66.7676, (CH2)OH-CHOH. 1C), (63.9486, 1C), (~49-48, N-(CH2)-CH2, 1C), (32.43828, 1C), (27.7626, 1 C), (27.3113, 1C), (23.1854, 1C), (14.2760, CH3, 1C).

2,3-dihydroxypropyl dihexylamines (VIII):^{1}H NMR (400 MHz, 50:50 vol% $CDCL_3$:CD_3OD): δ (3.7578-3.6796, N-CH2-(CH)OH-CHOH, 1H, m), (3.5403, OH(CH2)-CHOH, 2H, d), (2.5872-2.3816, 2xR-(CH2)-N-(CH2)-Gly, 6H), (1.5272-1.3757, 2xR-(CH2)-CH2, 4H, m), (1.3657-1.2142, 2xCH3-(CH2)3-CH2, 12H, m), (0.8751, 2xCH3, 6H, t, J=6.84 Hz)

2,3-dihydroxypropyl dihexylamines (VIII): ^{13}C NMR (400 MHz, 50:50 vol% $CDCL_3$:CD_3OD): δ(68.6673, CH2OH-(C)OH-CH2), 1C), (66.2009, HO-(C)H2, 1C), (58.6721, Glyc-(CH2)-N-2R, 1C), (55.4269, Gly-N-2x(C)H2-R, 2C), (32.3872, 2xCH2, 2C), (27.7433, 2xCH2, 2C), (27.3396, 2xCH2, 2C), (23.2055,2xCH2, 2C), (14.3332, 2xCH3, 2C)

A.3.2 NMR spectroscopy spectras

This section shows some NMR spectras from the results that are representative for the different categories. The NMR spectra for 220 °C is a typical NMR spectra for most of the trials in the temperature, catalyst, GC eq. and cat eq. screenings.

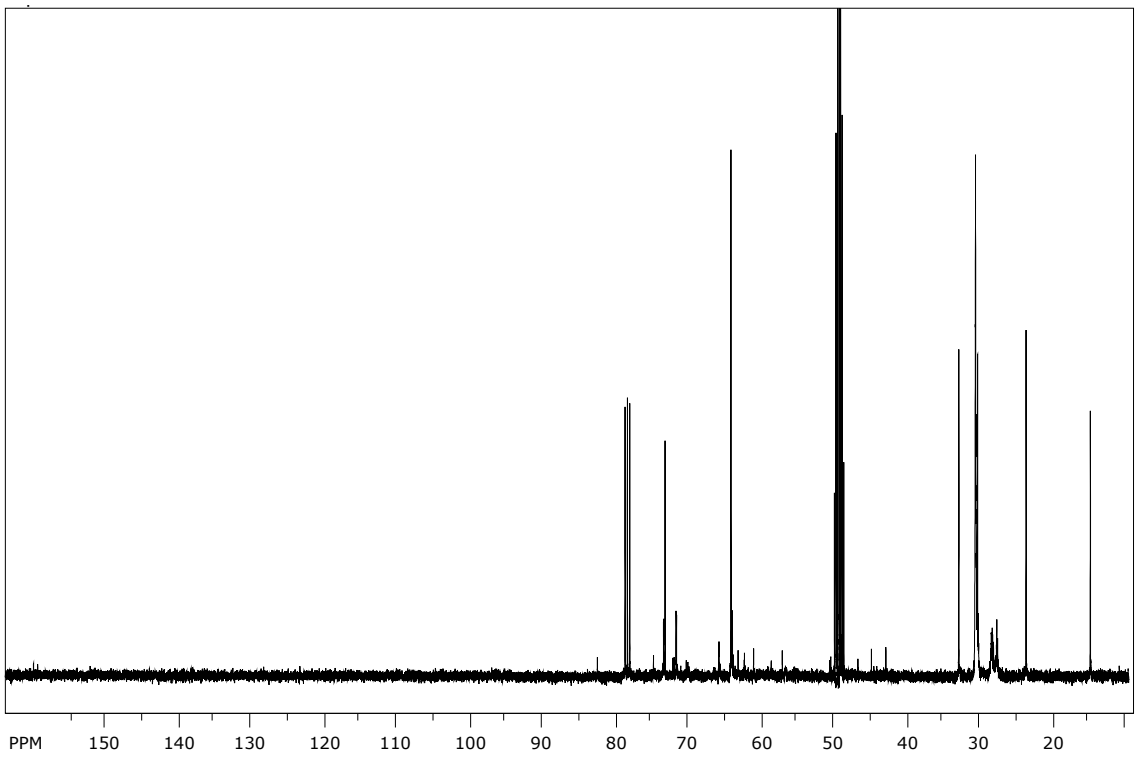


Figure A.2: This plot shows the ^{13}C NMR spectrum for 230 °C section 4.2.

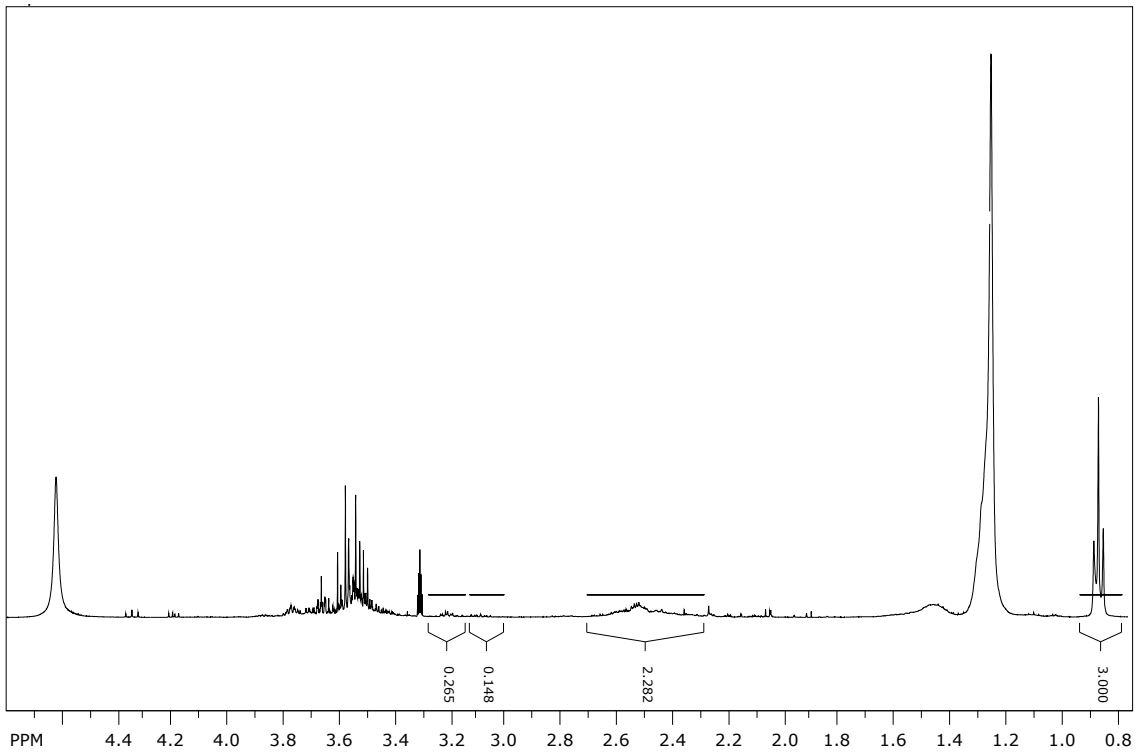


Figure A.3: This plot shows the ^{1}H NMR spectrum for 230 °C section 4.2.

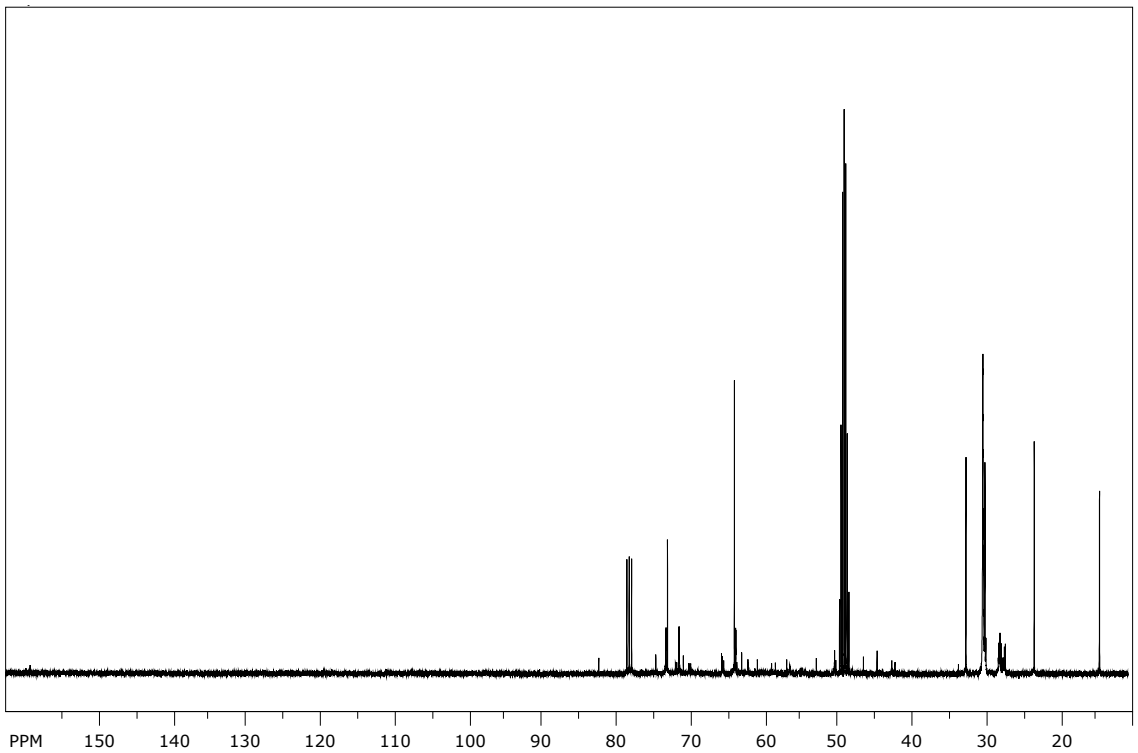


Figure A.4: This plot shows the ^{13}C NMR spectrum for 220 °C section 4.2.

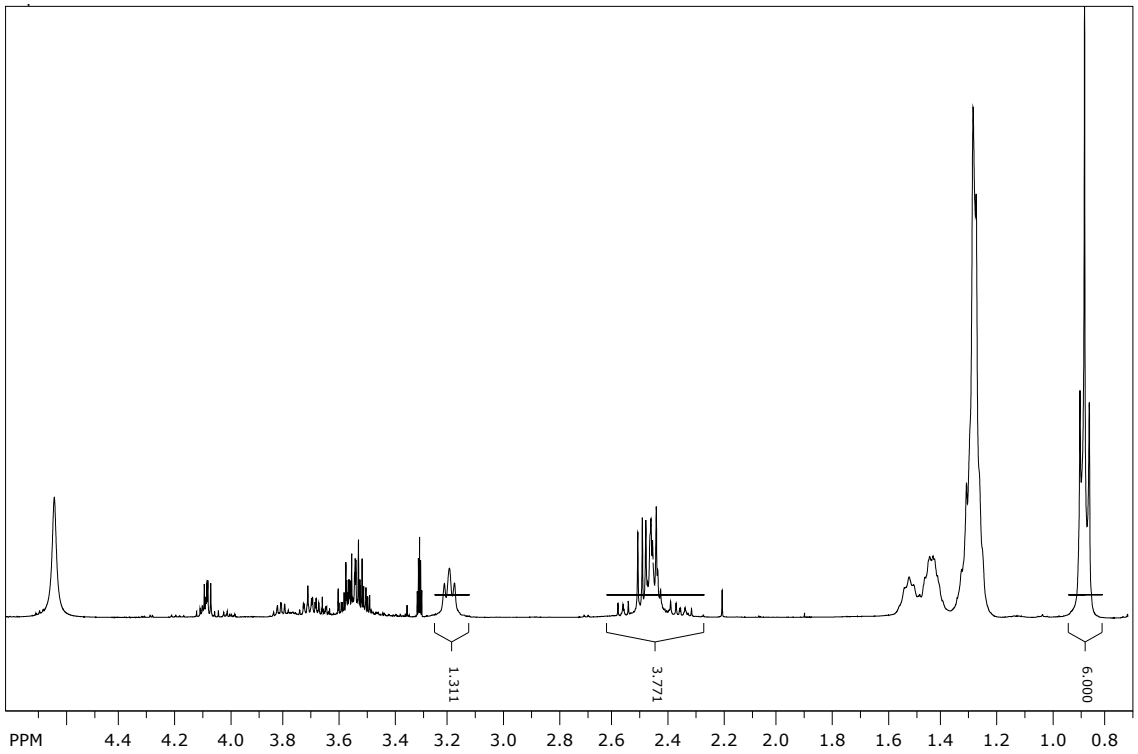


Figure A.5: This plot shows the ^{1}H NMR spectrum for synthesis with secondary FA and GC with $Ca(OH)_2$ as catalyst section 4.7.

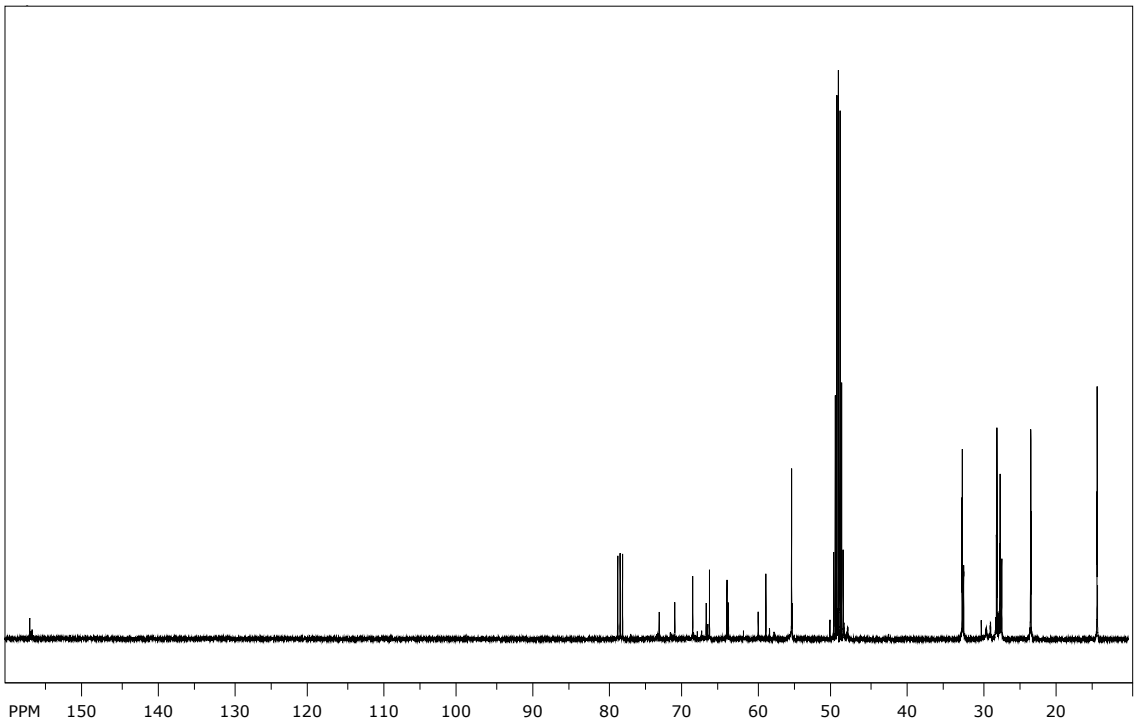


Figure A.6: This plot shows the ^{13}C NMR spectrum for synthesis with secondary FA and GC with $Ca(OH)_2$ as catalyst section 4.7.

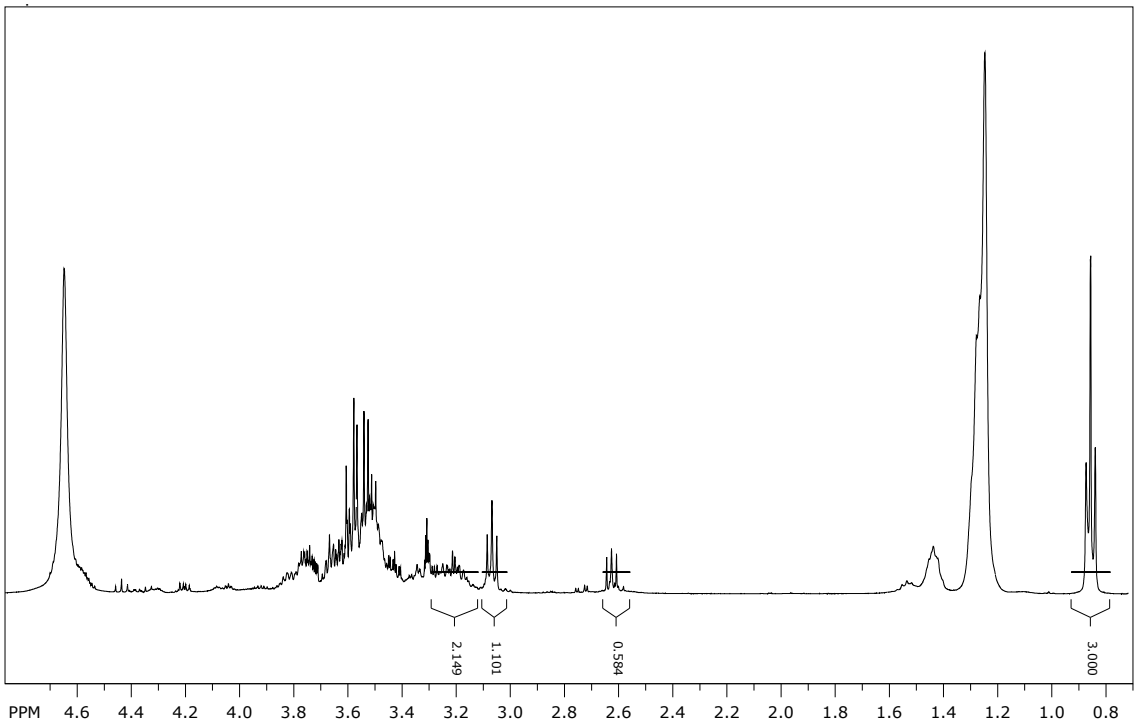


Figure A.7: This plot shows the ^{1}H NMR spectrum for the synthesis with glycerol, urea and primary FA seen in section 4.6.

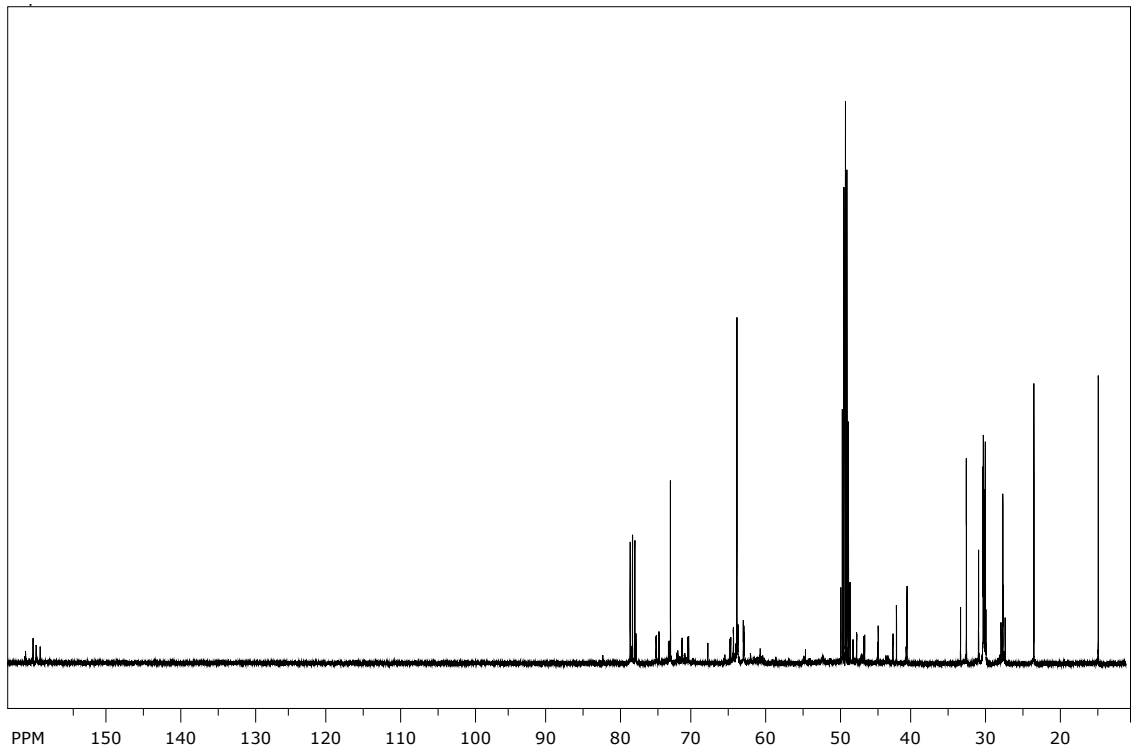


Figure A.8: This plot shows the ^{13}C NMR spectrum for the synthesis with glycerol, urea and primary FA seen in section 4.6.

A.4 Synthesis

This section summarizes reaction procedures for the investigated reactions. The materials used was 98 % Dodecylamine, 99 % decylamine, dihexylamine 99+%, 99 % ZnO, 97 % $Ca(OH)_2$, urea 99.5 % and NaOH in water 50 %. Glycerol and GC was synthesized on site and was assumed to be 100 %.

A.4.1 Reaction between GC, primary FA and $Ca(OH)_2$ at temperatures 190-230 °C

Alkylation of primary FA with GC was done by mixing, GC (25.52 g, 0.22 mol, 2 eq.), dodecylamine (20.53 g, 0.11 mol, 1 eq.) and $Ca(OH)_2$ (2.41 g, 0.03 mol, 0.27 eq.) and heating the mixture in a round-bottom flask with reflux condenser at the indicated temperature (190-230 °C) for 6 h. The reaction mixtures were analyzed with NMR spectroscopy.

A.4.2 Reaction between GC, primary FA and $Ca(OH)_2$ at temperatures 150-190 °C

Alkylation of primary FA with GC was done by mixing, GC (25.413 g, 0.22 mol, 2 eq.), decylamine (16.925 g, 0.11 mol, 1 eq.) and $Ca(OH)_2$ (2.392 g, 0.03 mol, 0.29 eq.) and heating the mixture in a round-bottom flask with reflux condenser at the indicated temperature (150-190 °C) for 4 h. The reaction mixtures were analyzed with NMR spectroscopy.

A.4.3 Hydrolysis of carbamates

Samples from temperature screening at 210 °C from section 4.2 and for 4 equivalents of GC from section 4.3 where hydrolyzed. Before hydrolysis, $Ca(OH)_2$ was removed from the sample for temperature screening at 210 °C. This was done by precipitating the catalyst in IPA followed by filtration and evaporation. Before hydrolysis, the amount of carbamates (IV and III) in the sample was determined with NMR spectroscopy. 5 eq. och NaOH was to be added in relation to carbamates for the hydrolysis. Since the sample with 4 GC eq. had more carbamates, more NaOH needed to be added. For 4 eq. of GC, 2.58 g of sample (1 eq. of carbamate) was added to NaOH (0.85 g, 0.011 mol, 5 eq.) in 5.06 g ethanol and 4.8 g water. For 210 °C, 20.35 g of sample (1 eq. carbamate (IV and III)) was added to NaOH (7.13 g , 0.089 mol, 5 eq.) in 40.17 g ethanol and 33.88 g water. The samples where hydrolyzed for 3h at 80 °C. NMR and GC-MS/FID was taken.

A.4.4 MgO and ZnO catalyst screening

Alkylation of primary FA with GC and ZnO was done by mixing GC (8.52 g, 0.07 mol ,2 eq.), dodecylamine (6.84 g,0.04 mol , 1 eq.) and ZnO (0.89 g, 0.01 mol, 0.30 eq.) in a vial reactor. Alkylation of primary FA with GC and MgO was done by mixing GC (8.51 g, 0.07 mol ,2 eq.), dodecylamine (6.82 g,0.04 mol , 1 eq.) and

MgO (0.44 g,0.01 mol, 0.30 eq.) in a vial reactor. The vials were slowly heated up to 210 °C and was reacted for 6 h. NMR spectroscopy and GC-MS/FID was taken.

A.4.5 Reaction between glycerol, urea, primary FA and $Ca(OH)_2$

Alkylation of primary FA with urea, glycerol and $Ca(OH)_2$ was done by mixing in a three necked round-bottom flask attached to a reflux condenser by mixing decylamine (15.73 g, 0.1 mol, 1 eq.), glycerol(18.42 g, 0.2 mol, 2 eq), urea (25.52 g, 0.41 g, 4 eq.) and $Ca(OH)_2$ (2.22g, 0.03 mol, 0.3 eq.). This procedure was done by slowly heating up the mix of glycerol, FA and half of the urea up until 140 °C, where the rest of urea was added. It was reacted at 140 °C for 1.h. After that, the yield of IV was 90 %. After that, the temperature was increased 10 °C every hour from 150-190 °C. The urea was added in two sections one half before heating and one at 140 °C. NMR spectroscopy and GC-MS/FID was taken.

A.4.6 Reaction between GC, secondary FA and $Ca(OH)_2$

Alkylation of secondary FA with GC and $Ca(OH)_2$ was done by mixing GC (11.38 g, 0.10 mol ,2 eq.), dihexylamine (8.93 g, 0.048 mol , 1 eq.) and $Ca(OH)_2$(1.07 g, 0.014 mol, 0.30 eq.) in a round-bottom flask attached to a reflux condenser. The reagents were slowly heated up to 160 °C and was reacted for 3 h. Afterwards, the temperature was increased to 170 °C and reacted for 1 h, following reaction at 190 °C for 2 h. In total the synthesis was 6 h.

A.4.7 Reaction between primary FA, GC and $Ca(OH)_2$ at different $Ca(OH)_2$ concentrations

Alkylation of primary FA with GC at different $Ca(OH)_2$ concentrations was done by mixing GC (8.62 g, 0.07 mol ,2 eq.), dodecylamine (6.80 g, 0.036 mol , 1 eq.) and $Ca(OH)_2$ ((0.42, 0.54 and 0.68 g), ($5.50 \cdot 10^{-3}$, $7.10 \cdot 10^{-3}$,$8.90 \cdot 10^{-3}$ mol), (0.15, 0.20, 0.25 eq.)) and reacting them for 6 h at 210 °C in vial reactors. The trial with no catalyst was done 2 times larger and reacted for 6 h at 210 °C in a round-bottom flask attached to a reflux condenser.

A.4.8 Reaction between primary FA, $Ca(OH)_2$ and GC at different GC equivalents

These reactions were performed at 210 °C in vial reactors for 6 h. 1 eq. GC was done my mixing GC (4.24 g, 0.036 mol, 1 eq.), decylamine (5.69 g, 0.036 mol, 1 eq.) and $Ca(OH)_2$ (0.81 g, 0.01 mol, 0.3 eq.). For 4 and 6 eq., GC ((17.01 g, 12.77 g), (0.14 mol, 0.11 mol), (4, 6 eq.)), dodecylamine ((7.12 g, 3.74 g), (0.04 mol, 0.02 mol), 1 eq.) and $Ca(OH)_2$ ((0.83 g, 0.43 g), (0.01 mol, $5.60 \cdot 10^{-3}$), 0.3 eq.). The reaction needed to be scaled down for increasing amounts of GC eq. to prevent overflowing the reactor.

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