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Department of Chemical and Forensic Sciences

Improving Mixing Properties of Biodiesel Substrates and Their Flow Properties: Molecular Dynamics studies

by

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Dedication

This thesis is dedicated to my late fathers, ***Gabautlwane Motshubi (grandfather)*** and ***Andrew Phetogo Gabalebe (father)***, who always motivated me and encouraged me to work smarter and harder.

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ABSTRACT

Biodiesel is created through a transesterification reaction in which excess methanol reacts with triglycerides in the presence of a catalyst. The reaction is rather slow due to the poor miscibility of triglycerides with methanol, which ultimately increases production costs. Once produced, biodiesel has poor cold flow properties and lacks oxidative stability. These poor cold flow properties make it challenging to use FAMES during winter months as they tend to form gels, affecting both the engine's performance and durability. This thesis sought solutions to two major limitations of biodiesel production processes slow transesterification during production and poor cold flow properties of neat biodiesel. The first section focused on interactions occurring in binary mixtures of triglycerides and commonly used cosolvents. The structural aspects of these binary mixtures are the focus of the section. The second part was on the interactions in the ternary mixtures, focusing on quantifying the miscibility of methanol in triglycerides in the presence of cosolvents using thermodynamic parameters derived from molecular dynamics simulations. Finally, the third section focused on improving flow and oxidative properties by converting biodiesel to hydrocarbons.

This study used triolein, a common triglyceride in oils, as a model fatty acid methyl ester. The structural aspects of six triolein and co-solvent mixtures were investigated to understand the interactions between triglycerides and cosolvents better. The cosolvents used in this study were tetrahydrofuran, hexane, gamma valerolactone, cyclopentyl methyl ester, diethyl ether and dioxane. The results of 100 ns simulations at constant temperature and pressure to simulate mixing show that all binary mixtures are largely unmixed in the first 10 ns and fully mixed at 100 ns except for mixtures containing gamma valerolactone and dioxane. Some solvents interacted strongly with the polar part of triolein, while others interacted strongly with the aliphatic part. Solvation indicators also included the radial distribution functions and clustering of the solvents around triolein. Cosolvents were also found to influence the conformation of triolein molecules. Triolein favoured a propeller conformation in the presence of solvents that solubilize it and adopts a trident conformation when there is little or no solubilisation. The results show that the best solvent for solubilizing triolein is tetrahydrofuran, followed by cyclopentyl methyl ether, diethyl ether, and hexane. The solubility of 1,4-dioxane was found to increase with

temperature. A solvent's miscibility with triolein is aided by its ability to interact with both the polar and non-polar parts of the triolein.

In the case of ternary mixtures (triolein/methanol/cosolvent), the Flory-Huggins theory of solutions was applied using molecular dynamics derived parameters. The binary interaction parameters (χ_{ij}), Gibbs Free energy (ΔG^m) and chemical potentials of the components ($\Delta\mu_i$) were calculated to study the mixing behaviour). Along the phase boundary, the binary interaction parameters between methanol and cosolvent remain relatively constant. The Gibbs free energy of mixing (ΔG^m) in this region shows both positive and negative values, indicating the presence of both mixed and unmixed phases. As expected and consistent with experimental data, ΔG^m for the systems decreases as one moves from the two phase to single phase part of the ternary system. The activities calculated from Flory-Huggins model were in good agreement with the commonly applied UNIFAC model.

The conversion of methyl palmitate to hydrocarbons was studied using Reactive Force Field (ReaxFF) molecular dynamics as a model to improve the flow properties of biodiesel. α -NiMoO₄, β -NiMoO₄, and Ni₃Mo were used as catalysts. The results show that the reaction is initiated by the cleavage of the O-CH₃ bond, which results in the formation of C₁₆H₃₁O₂[•] and CH₃[•] radicals. After its formation, the C₁₆H₃₁O₂[•] radical is then decarboxylated to produce carbon dioxide and C₁₅H₃₁[•] radical. Through β -scission decomposition, this radical produces ethene which is one of the major products. The results also show that the reactions are faster in the presence of catalysts in agreement with experiment. With Ni₃Mo as a catalyst, there is evidence of the decomposition of CO₂ into CO and C₂H₄ into C₂H₂ and H₂. Overall, the β -NiMoO₄ catalyst performs better in terms of the conversion of methyl palmitate and formation of major products than α -NiMoO₄ and Ni₃Mo. All the catalysed and uncatalysed decarboxylation of methyl palmitate follows first-order kinetics, from which the activation energy (E_a) was determined. The presence of a catalyst reduced the activation of the reaction from 36.89kcal/mol in an uncatalyzed system to 25.66, 19.34, 15.32, 14.40, and 11.69 kcal/mol for the α -NiMoO₄ (110), β -NiMoO₄(110), α -NiMoO₄ (021), β -NiMoO₄ (021), and Ni₃Mo (101) catalyzed reactions, respectively. The Ni₃Mo catalyzed system has the lowest activation energy of 11.69 kcal/mol, which is comparable to experimental results of 10.11kcal/mol.

CHAPTER 1

INTRODUCTION

Global energy needs and consumption are increasing daily because of the increase in modernization and industrialization. The main sources of energy to meet this demand can be divided into three main categories being, fossil fuels, renewable sources, and nuclear sources. Fossil fuels include natural gas, petroleum, and coal, while renewable sources include, biomass, solar, wind and hydroelectricity[1,2]. According to the International Energy Agency (IEA) report of 2020, the dependence on fossil fuels is much higher compared to other sources of energy as shown in Figure 1[3].

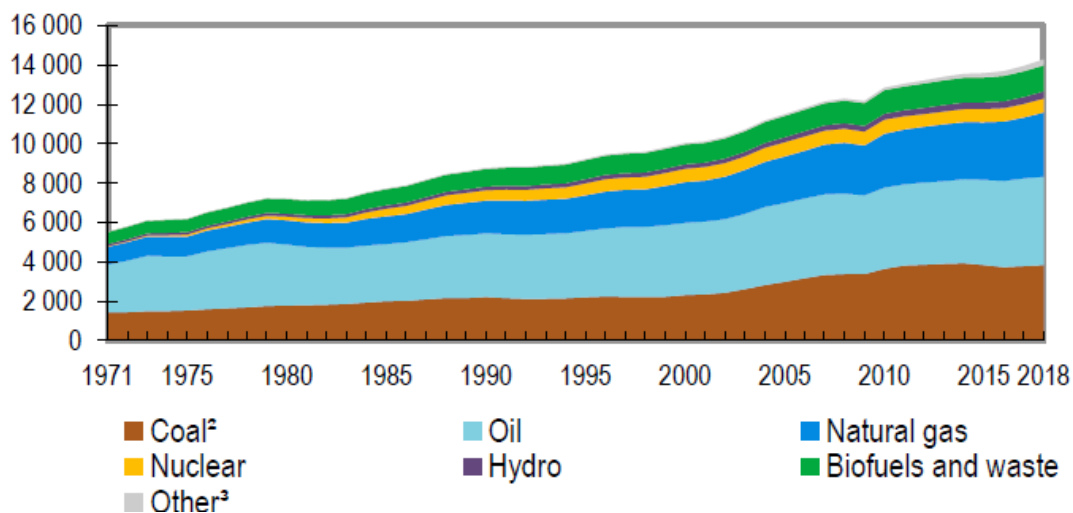


Figure 1: Comparison of the main sources of energies from 1971 to 2018. Adapted from IEA statistics [3]

Africa, just like the rest of the world is currently experiencing serious energy crisis. While the energy crisis has always been present, the economic recovery following Covid-19 restrictions has exacerbated the situation[4]. The geopolitical tensions also resulted in the major suppliers of petroleum fuels cutting the supply of fuel drastically causing a mismatch between supply and the demand, with the demand far exceeding the supply. This resulted in the rapid increase in the prices. Natural gas costs have risen dramatically since early 2021, with prices averaging more

than 100 €/MWh between October 2021 and mid-2022, over seven times more than before Covid-19, when prices were around 15 €/MWh[5]. The rise in the price of fossil fuels has resulted in an increase in the overall cost of living.

The fossil-based fuels are not renewable and are rapidly depleting; they will not be sufficient to sustain future generations. According to recent predictions, they will not last beyond 2050. In addition, the processing of fossil fuels and their combustion releases gases like carbon dioxide, methane, sulphur dioxide, nitrous oxides and ozone into the atmosphere. The accumulation of these gases in the atmosphere forms a blanket that traps heat energy from the sun and does not allow it to escape, causing global warming.

1.1 Global warming

Global warming is described as an increase in the average temperature of the Earth's atmosphere over time. It is caused by increasing emissions of greenhouse gases including carbon dioxide (CO₂), water vapour (H₂O), methane (CH₄), nitrous oxides (N₂O), ozone (O₃), chlorofluorocarbons (CFCs) and sulphur dioxide (SO₂) to the atmosphere. These greenhouse gases trap heat energy from the sun and radiate that heat back to earth causing an increase in the temperature.

Thirty billion tons of CO₂ are emitted per year of which twenty percent is from the United States [6]. Shown in Figure 2 is the carbon dioxide emissions from different regions from 1971 to 2018[3]. Clearly the emissions are not going down but increasing, with China and Organization for Economic Co-operation and Development (OECD) countries being the major contributors. Africa is one of the regions mostly affected by climate change, even though it only contributed a mere 4% of global carbon dioxide (CO₂) emissions in 2019.

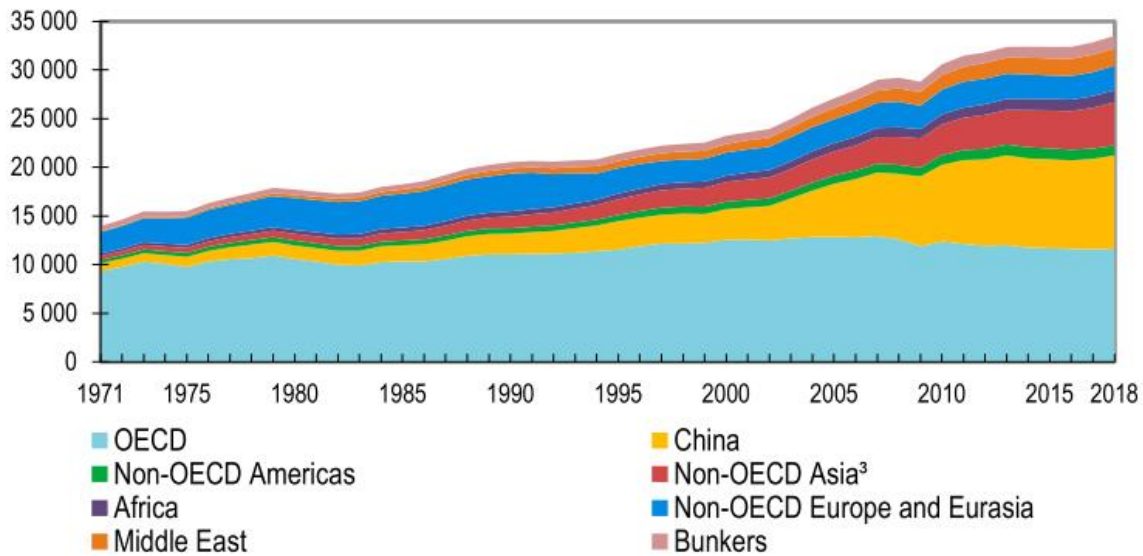


Figure 2 : Global carbon dioxide emissions from 1971 to 2018 adapted from [3]

Increase in earth temperature has dire effects to human populations and all the ecosystems in general. The increase in global temperature causes frequent heatwaves which causes an increase in heat strokes which at times result in loss of life for both humans and animals. Global warming is also causing severe weather conditions, which is causing damage to homes. These adverse weather conditions include, to name a few, wildfires, flooding, storms, and cyclones. Drought and water scarcity are affecting food production, resulting in food shortages. Food shortages cause hunger and starvation, which can lead to death. Therefore, there is a need to find alternative sources of energy that will meet the energy demand without causing global warming. These energy sources must be carbon-neutral and must produce no greenhouse gases.

1.2 Renewable sources of energy

Renewable energy sources are those that will not deplete and do not harm the environment. Biomass, wind, solar, and hydrothermal energy are the most common renewable energy sources. The price of the alternative sources has continued to fall while that of fossil fuels has continued to fluctuate in the upward direction, making them more accessible to the masses. Discussed below are the advantages and disadvantages of different renewable sources of energy.

1.2.1 Solar energy

Solar energy is one of the most abundant renewable resources which is also carbon neutral. It is available almost everywhere on the earth. The solar energy systems can be classified into two main categories being photovoltaic cells and solar thermal systems. In photovoltaic cells sunlight is converted to direct current electricity using semi-conductors. Most semi-conductors in use today have poor efficiency. Researchers are currently working hard to find ways to improve the efficiency of semi-conductors. Morphology, surface area, and quantum scale behavior studies have resulted in the development of new photovoltaic devices. This has helped in improving the efficiency of such devices[6]. Figure 3 shows power conversion efficiencies of some photovoltaic devices currently being used and those under development.

In solar thermal systems, sunlight is used to heat water which is then used to generate steam. The steam is then used to drive turbines that generate electricity. Solar thermal technology is a more efficient use of solar energy than photovoltaics and accounts for 7% of the renewable thermal energy[7]. The primary source of solar energy, the sun, is not always available, especially at night or when the sky is cloudy, which is a major drawback. To address this issue, the energy generated by solar rays, either electricity or heat, could be stored directly or after conversion to other energy forms for later use[7–10].

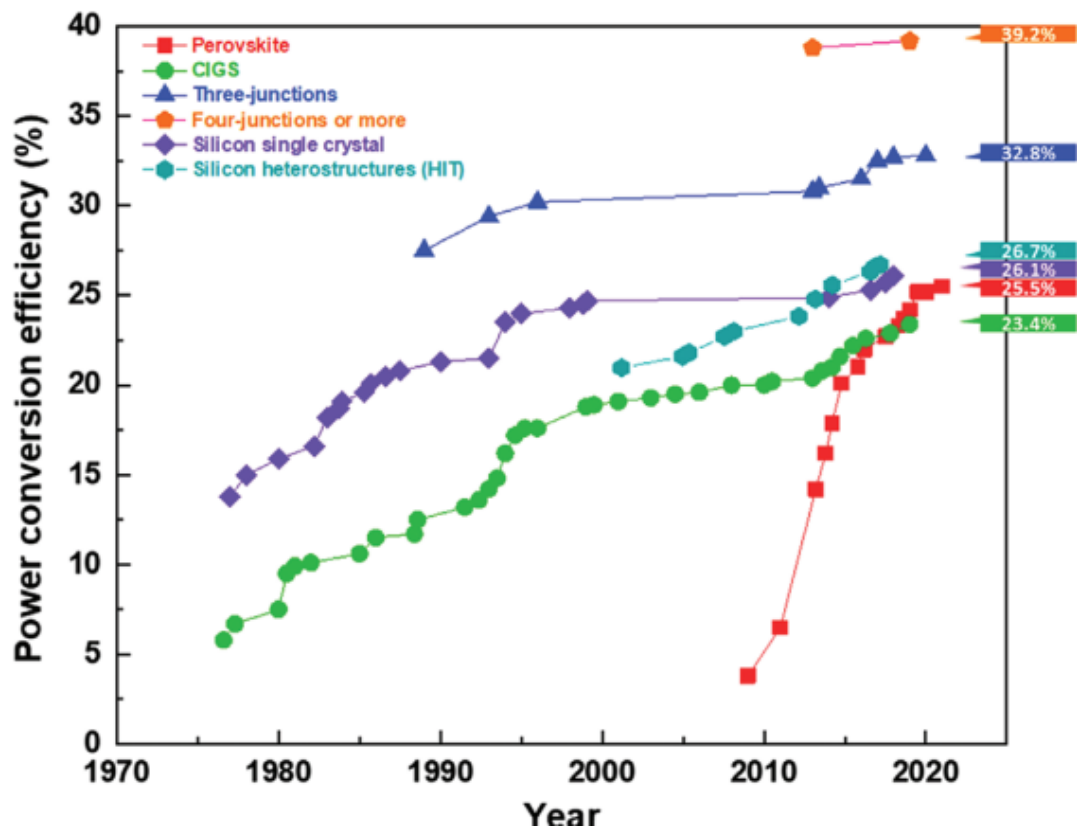


Figure 3: Power conversion efficiencies of different Photovoltaic materials[11].

The advantages of this source of energy include.

- It is renewable, and it won't run out as long as the sun exists.
- It is a clean source of energy that does not produce greenhouse gases such as carbon dioxide, nor does it produce any pollutants like sulphur dioxide or particulate matter.
- By lowering the quantity of electricity purchased from the grid, solar energy can dramatically reduce electricity prices for businesses and homes.

The disadvantages of solar energy include the following,

- Solar energy generation depends on sunlight, so it only produces electricity during the day and is less effective on cloudy days or at night. Energy storage systems or backup sources are needed for power after sunset.
- Solar energy systems often need batteries for energy storage when the sun isn't shining, but these batteries can be expensive and add significant costs to the overall system.

- Solar panel installation and acquisition can come with a hefty upfront cost that covers labour, inverters, wiring, and panel costs.
- Solar panels usually have an energy conversion efficiency of 15-22%, which means that a lot of captured sunlight isn't converted to electricity. Although improving, their efficiency still lags behind other energy generation technologies.

1.2.2 Hydroelectric energy

Hydroelectric energy uses moving water to drive turbine which in turn generates heat and electrical energy. This kind of energy has been used for centuries since the 1770 industrial revolution to grind millets and flour. The electric generator, coupled with hydraulics, was developed in the late 19th century to meet electricity demands resulting from the expansion of industrial revolutions. New hydroelectric power plants are still being built to meet energy demands. The world's three largest dams include Hoover Dam, Grand Coulee Dam, and Three Gorges Dam. Hoover Dam was built in 1936 and produces 1345 MW of energy. Grand Coulee Dam, built in 1942, produces 6089 MW, while Three Gorges Dam in China, which was built in 2008, produces the most energy at 22.5 GW. Hydroelectric energy is the main supplier of energy in some countries. It supplies about 85% of energy in Brazil, Norway, and Democratic Republic of Congo (DRC). Table 1. 1 shows the production of hydroelectric energy and how it is continuing to grow.

Table 1. 1: The summary of hydroelectric energy generated from different regions of the world. It shows the hydroelectric potential, installed stations and the dams that are still under construction. Adapted from reference [2]

Region	Gross Theoretical Potential	Installed Capacity	Under Construction
	TWh/y	GW	GW
North America	5817	141.2	0.9
South America	7533	114.1	18.3
Europe	6747	172	16.9
East and North Africa	304	21.3	1.2
Sub Saharan Africa	3583	65.7	16.6
Asia	15666	106.3	69.4

There are several ways through which electricity is generated using water. The water flowing upstream can be used to drive turbines which in turn generates electricity. Tidal waves from the oceans can also be used to drive turbines. Dams also help in creating up and down movement of water which also generates electricity.

The advantages of hydroelectric energy include the following.

- There are no carbon dioxide emissions.
- The water is stored at lower cost, then it is used to generate clean and low-cost energy.
- Waterfalls and dams are tourist attractions sites and help in creating employment opportunities for locals.

The disadvantage of hydroelectric energy include.

- The new dams interrupt the flow of rivers and may result in less water being available to local inhabitants of the region. This results in altering ecosystem and loss of land.
- Water reservoirs may have limited flow of water in some months this affects the electrical output.
- There are also methane emissions caused by anaerobic decay of plants in the dams.
- Animals and local people might be forced to relocate to make way for dam construction.
- And finally, there is risk of flooding caused by overflowing or bursting dams.

1.2.3 Wind energy

Wind energy is a renewable source of energy that has been used since before the industrial revolution. For centuries, kinetic energy from air movement has been used to pump water, grind agricultural grains, and propel sail boats and sail ships. This kinetic energy is now converted to electrical energy by a wind turbine, as shown in Figure 4.

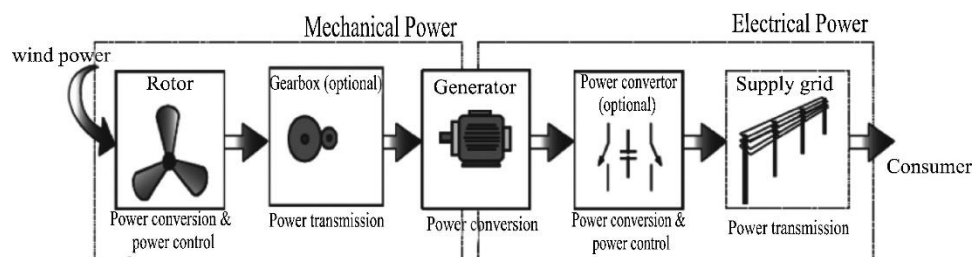


Figure 4: Schematic diagram showing how kinetic motion of wind is converted to Electrical power using turbines. Adapted from Panwar et al., reference [12]

Since the 1980s, wind-generated electricity has grown at a rate of 24% per year. Figure 5 depicts the global growth of wind energy, with China's production increasing from 1.9% to 28.7%.

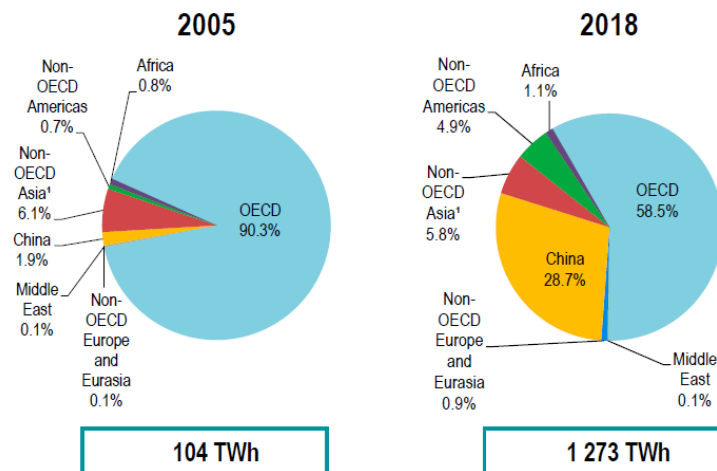


Figure 5: The change in the generation of wind energy between 2005 and 2018[3].

The advantages of this source of energy includes.

- The wind industry is less sensitive to price volatility compared to natural gas and coal fuel. Shifting to wind energy can lead to lower energy prices.
- It does not produce carbon dioxide or any greenhouse gases.

The disadvantages include,

- Wind is difficult to predict, making it difficult to ensure a continuous supply of electricity.
- Electricity generated from wind energy is location-specific, meaning it cannot be transported like fossil fuels or nuclear energy. It can only be used in the same location where it was produced. However, the generated energy can be stored in very expensive batteries.
- The rotating blades of turbines cause noise pollution.
- Birds and bats are killed when they collide with rotating blades.
- The moving turbines also generate turbulences which cause an increase in temperature at night for communities living near wind farms[13]

- Animals and local people are sometimes relocated to make way for new wind farms.

1.2.4 Biomass

Biomass is another alternative source of energy that is derived from organic matter. The biomass can be converted into solid, liquid, and gaseous biofuels. The sulphur content of biomass is low. It is widely regarded as CO₂ neutral since plants remove CO₂ from the atmosphere through photosynthesis during their growth, which is then released again during fuel combustion. The main sources of biomass include woods, agricultural wastes and algae from rivers and oceans. The biomass can be upgraded to more practical fuel using the three major conversion routes being, chemical, thermal and biological. In biological conversion, biomass is converted to bioethanol by fermentation or to biogas by anaerobic digestion. Thermal upgrade includes heating in the absence or presence of oxygen. Thermal upgrade processes include gasification and pyrolysis. In gasification, biomass is converted to syngas (CO + H₂) by heating it at a temperature between 800-900 °C under controlled amount of oxygen. In pyrolysis, biomass is converted to several fuels including methane, charcoal, and hydrogen by heating it in little or no oxygen at temperatures ranging from 400 to 500 °C. Finally, biomass can be upgraded by chemical means. An example is the conversion of animal fats and plant oils to biodiesel using the reaction known as transesterification[14–16]. Biodiesel production will be discussed in detail in section 1.3.

The advantages of biomass derived energy include the following.

- It is a renewable source of energy. This is because the main source of biomass is plants and new plants can easily be grown to replace used plants in relatively short time.
- The use of biomass helps in reducing organic waste. Organic waste produces greenhouse gases like carbon dioxide and methane during decomposition. Turning this biomass into biofuels clears landfills and provides fuel at the same time.
- When biomass is burned, it produces minimal amounts of carbon dioxide and other greenhouse gases such as SO_x and NO_x.

The disadvantages include,

- The cost of turning biomass into fuels is very high.
- A lot of space is required for industrial plants which processes biomass into fuels and in planting new trees that replaces cut plants.

- Natural ecosystems are affected by conversion of biomass into fuels. These include deforestation and loss of fertile soils.
- Compared to petroleum fuel biomass derived fuels have lower energy density

1.2.4.1 Biofuels

Biofuel is a term used to describe liquid or gaseous transportation fuels that are mainly derived from biomass, which includes liquid fuels like ethanol, methanol, biodiesel, and gaseous fuels like hydrogen and methane. Liquid biofuels are primarily used to power vehicles, but they can also be used to power engines or fuel cells for electricity generation. Figure 6 depicts the predicted global growth and demand for biofuels in 2021 and 2027. It shows that ethanol is in higher demand than other biofuels, such as biodiesel, renewable diesel, and bio-jet, on a volume basis. This trend is expected to continue in 2027. When it comes to energy demand, the total energy demand met by ethanol is predicted to be slightly higher in 2027 than it was for 2021. This is because the energy content of the three other biofuels is 60% higher than that of ethanol, their demand is expected to reach 2.5 EJ i.e ($1\text{EJ} = 1 * 10^{18}\text{J}$), which is ahead of 2.4 EJ for ethanol[17]. Biodiesel has a higher energy density than ethanol, making it a more attractive replacement for current diesel engines. It can also be used in the transportation sector with little or no modification to engines. However, biodiesel has limitations that are discussed in detail in the following subsection.

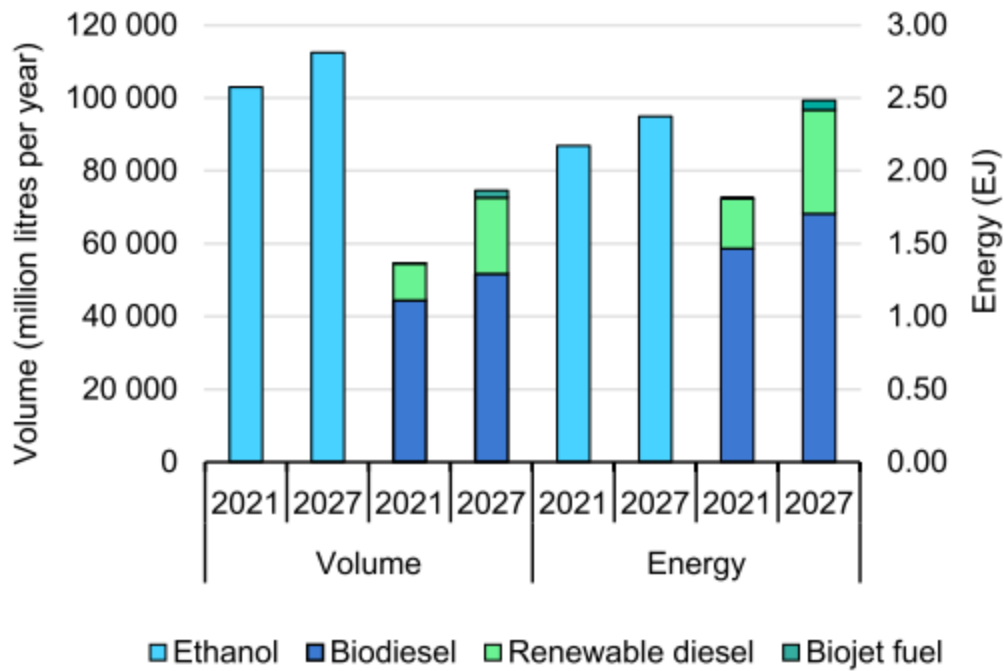


Figure 6 : The global biofuel growth and demand [17]

1.3 Biodiesel

Animal fats and plant oils can easily be used as an alternative source of energy. The main problem with these oils and fats is that they are very viscous and cannot be used in the engines in their current form, so they are converted to biodiesel to reduce viscosity. Biodiesel, also known as fatty acid methyl esters (FAMEs) is a renewable fuel that is made from reacting vegetable oils or animal fats with short chain alcohols. The reaction is known as transesterification[18,19]. Transesterification is always conducted in the presence of a catalyst (which can either be acidic, basic or enzymatic)[20–22]. Biodiesel is renewable because biological resources such as plant biomass and animal waste are used as feedstock. Besides being renewable, biodiesel is very attractive as a fuel because it has less air pollutants per net energy than fossil fuels. It is also non-toxic, biodegradable and has high energy efficiency. It has high cetane number, no aromatics and no sulphur when compared to petroleum diesel[23]. It also has a higher flash point than petroleum fuels. These qualities contribute to a reduction in the emissions of pollutants including carbon monoxide, sulphur dioxide, and hydrocarbons that are present in the exhaust gases of diesel fuel derived from petroleum. Because the ester molecule contains an oxygen atom, it burns

more effectively and produces less carbon monoxide as a result. The ester group also makes biodiesel to be biodegradable.

1.3.1 Transesterification

Transesterification is class of organic reactions in which an ester is transformed to another ester by interchanging of alkoxy moiety of an alcohol with that of an ester[24]. This reaction is sometimes known as alcoholysis. In this reaction triglycerides are reacted with a short chain alcohol (methanol, ethanol or propanol) in presence of a catalyst to form alkyl esters [7]. Glycerol and sometimes soap are also produced as by-products of the reaction. The reaction is usually conducted in excess methanol to push the reversible reaction towards formation of biodiesel. Methanol is commonly used as a short chain alcohol because of its availability and the fact that it is cheaper than other alcohols. The reaction temperature is between 40°C and 80°C and constant stirring is done to disperse the oil in methanol. The reaction can take place in the presence of catalyst, with potassium or sodium hydroxide being preferred catalysts. The overall equation of reaction is shown in Figure 7.

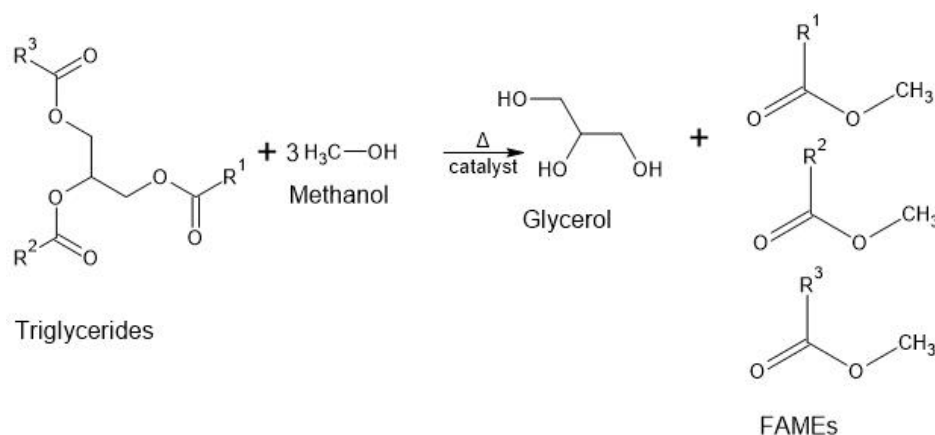
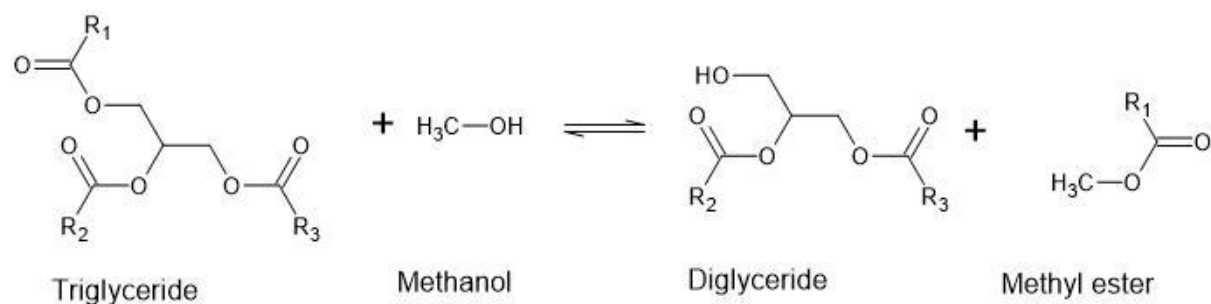


Figure 7 :A simplified transesterification reaction [5].

The reaction takes place in three consecutive steps that are reversible. The first step in this mechanism involves the reaction of methanol with triglyceride leading to the formation of a diglyceride as shown in scheme 1. In the second step, the diglyceride produced in step 1 reacts with more methanol to form a monoglyceride. Finally, the monoglyceride is converted to glycerol while another methyl ester is formed. Generally, one triglyceride molecule reacts with

three molecules of alcohol, producing three molecules of fatty acid methyl esters (FAMES or biodiesel).



Scheme 1: Formation of diglyceride from a triglyceride

1.3.1.1 Biodiesel feedstock selection

Feed stock for biodiesel production can be categorized as first-generation, second-generation, and third-generation feedstock. The first-generation feedstock includes those mainly from edible vegetable oils like palm oil, coconut oil, soybean oil, sunflower oil, and olive seed oils to mention a few[15,25–27]. The use of these oil is raising food versus fuel debate which is a serious concern especially in developing countries where there are already food shortages. Using fertile land for production of oil and converting it to fuel raises food security concerns[28]. The second generation feedstocks include non-edible seeds like jatropha, neem seeds, tobacco seeds, mahua, animal fats and used waste vegetable oils[29–33]. Although not in direct competition for human consumption, they can be used for animal consumption. The third-generation biodiesel feedstocks, such as algae and sea weed[34], can help overcome the limitations of using first- and second-generation feedstock because they are not consumed by humans or animals. They can produce a lot of bio-oil per unit area when compared to traditional plant feedstock. Third-generation feedstock do not require high quality land to produce high quality biofuels[35].

1.3.1.1.1 Animal fat-based feedstock

Animal fat-based feedstock can be considered second-generation feedstock. Animal fats have low nutritional value, and their consumption is often associated with increased health risk. Although generally considered waste, they can still be used to feed animals, hence the classification as second-generation feedstock. Animal fats as feedstock are less expensive than vegetable oil-based feedstock and their preparation before transesterification only include simple step of rendering compared to complex extraction of oils from seeds. Biodiesel produced from

animal fat has high cetane value and a heating value that is closer to that one of petroleum diesel[36]. Some of the most commonly used fats in the production of biodiesel include beef tallow[21,33,37,38], poultry fat [39–41] and pork lard[32,38]. Mata et al.,[32,38] were able to produce biodiesel from beef tallow (TME) , pork lard (LME) and chicken fat (PME). They were able to achieve high yields of 76.8% of PME, 90.8% of TME and 91.4% of LME from a 2-hour transesterification reaction of the animal fat using potassium hydroxide as a catalyst. From their findings FAMES produced were able to meet the EN 14214 limits except cold filter plugging point (CFPP) which was higher in TME and moisture content which was higher in PME. Öner et al.,[36], tested biodiesel produced from beef tallow on the petroleum diesel engine, and found that its calorific value was slightly lower than that of petroleum diesel, but the engine power produced was comparable to that generated from petroleum diesel. Their findings also showed a significant reduction of emissions of carbon monoxide, oxides of nitrogen, sulphur dioxide and smoke by 15%,38.5%,72.7% and 56.8% respectively. They concluded that tallow biodiesel can be used in the current diesel engine with no modifications at all.

The major disadvantages of animal produced biodiesel are the poor cold flow properties and oxidative instability. This makes it very difficult to use during cold winter seasons and for a long-term storage. These properties are mainly due to the high composition of both saturated and unsaturated fatty acids methyl esters. Presented in Table 1. 2 is the fatty acid methyl ester composition from three animal fat produced biodiesel. The data shows that, tallow-based biodiesel suffers mainly from poor cold flow properties while chicken and lard biodiesel suffer mainly from poor oxidative stability.

Table 1. 2: Fatty acid methyl ester composition of different animal fats produced methyl esters.

FAMES	Tallow biodiesel (%)	Lard biodiesel	Chicken biodiesel	References
C14:0 (myristate)	2.72	-	-	[33]
C15:0 (Pentadecanoate)	0.86	-	-	[33]
C16:0 (palmitate)	25.35	28.12	19.82	[33,38,41]
C16:1 (Palmitoleate)	2.02	-	3.08	[33,41]

FAMES	Tallow biodiesel (%)	Lard biodiesel	Chicken biodiesel	References
C17:0 (heptadecanoate)	1.67	-	-	[33]
C18:0 (stearate)	34.70	11.62	6.09	[32,33,41]
C18:1 (oleate)	29.87	38.05	37.64	[32,41,42]
C18:2 (linoleate)	0.87	18.83	31.56	[33,38,41]
C18:3 (linolenate)	-	3.38	1.45	[38,41]
C20:0 (arachidate)	0.28	-	0.36	[33,41]
% Saturated	65.56	39.74	26.27	
% Unsaturated	34.44	60.26	73.73	

1.3.1.1.2 Plant oil-based feedstock

Both edible and non-edible plant seeds oils can be used as feedstock for biodiesel production making them fall into the first and second generation of feedstocks. The commonly used non-edible oils for transesterification include the oils extracted from *Jatropha curacas* [30,43–46], mahua [47,48], Karanja[49,50] , neem[51] and cottonseed oil[26]. The edible oils feedstock include sunflower[52], rapeseed oil[53], coconut[15], soybean oil[15,54] and palm oil[25]. Compared to edible oils, non-edible oils are toxic for both human and animal consumption, which makes them cheaper and their usage for fuel production eliminates fuel vs food debate[30,50]. They grow freely in nature and there is no need to set aside special land for their cultivation[55]. The main disadvantage of using them in biodiesel production is that they have high content of free fatty acids which leads to two step transesterifications using both acidic and basic catalysts[30]. Table 1. 3 shows biodiesel yields and reaction conditions for various plant oil-based feedstocks.

Properties of biodiesel produced from plant feedstock have comparable properties to petroleum derived fuels, like high calorific values and high cetane number[56,57]. Similar to animal-based feedstock, they suffer from poor flow properties and poor oxidative stability.

Table 1. 3: Summary of some transesterification reactions using plant oil-based feedstock.

Plant feed stock	Edible/ non-edible	Catalyst	Reaction conditions	yield	Reference
Sunflower oil	edible	NaOH	Oil:MeOH ratio (1:3-1:9) Time: 1-3hr Temp: 60°C	80%	[58]
Bitter almond oil	Non-edible	KOH	Oil: MeOH 1:3 Time: 1h Temp: 32°C	90%	[59]
Parsley seed oil	edible	CaO	Oil: MeOH 1:9.4 Time: 3h Temp: 59.3°C	92.1%	[60]
Jatropha	Non-edible	H ₂ SO ₄	Oil: MeOH 1:5 Time: 3h Temp: 60°C	99%	[29,30]
Palm oil	edible	KOH	Oil: MeOH 1:6 Time: 90min Temp: 60°C	90%	[52]
Soybean oil	edible	NaOH	Oil: MeOH 1:6 Time: 90min Temp: 30-70°C	90%	[61]
Rape seed oil	edible	KOH	Oil: MeOH 1:9 Time: 30min Temp: 30°C	97-98%	[53]
Mahua oil	Non-edible	H ₂ SO ₄ KOH	Oil: MeOH 1:3 Time: 1h Temp: 60°C	98%	[48]
Karanja oil	Non-edible	KOH	Oil: MeOH 1:6 Time: 1h Temp: 35,45 and 55°C	85%	[50]

Plant stock	feed	Edible/ non-edible	Catalyst	Reaction conditions	yield	Reference
Cotton oil	seed	Non-edible	KOH and NaOH	Oil: MeOH 1:6 Time: 1h-48h Temp: 60°C	90%	[26,62]

1.3.1.2 Catalysts

Catalysts used in the transesterification reactions can either be homogeneous or heterogeneous. Homogenous catalysts are the type where the oil and the catalyst are in the same phase while in heterogeneous catalysis the catalyst and oil are in different phases. The reaction can be catalyzed by strong bases, acids, and in some cases both acids and bases are used. Bases such as sodium hydroxides, potassium hydroxide and metal alkoxides have been used as catalysts for alcoholysis. The advantage of using NaOH/KOH is that the reaction is fast, 97% conversion usually happens in less than an hour [63–65], and it takes place at low temperature of 50-70°C. The main problem with base catalyst is that water is produced as a by-product, and this complicates the process because its presence leads to hydrolysis of FAMES and formation of soap, and this causes a decrease in the percentage yield. Potassium carbonate, sodium carbonate, boiler ashes, have also been utilized as base catalysts, yielding very high FAME yields. The use of carbonates has been found to minimize the formation of soap. This is because the carbonate reaction produces bicarbonates rather than water, which does not hydrolyze esters[45,65].

The transesterification process can also be catalyzed by acids like HCl, H₃PO₄, and H₂SO₄. Using acid catalysts has been found to lead to high yields of FAMES [10]. However, acid-catalyzed transesterification reactions are relatively slow compared to base-catalyzed ones[19,66]. Figure 8 shows the mechanism for base catalyzed transesterification of triglycerides. The first step is the production of an active species, RO⁻ (alkoxide ion) from the reaction of methanol and base catalyst. This is followed by the nucleophilic attack of RO⁻ to carbonyl group on the triglyceride which results in the formation of a tetrahedral intermediate, this intermediate then breaks down resulting in the formation of diglyceride and a FAME molecule. This sequence is repeated twice until glycerol is formed[67]. In acid-catalyzed reaction, the reaction starts with the protonation of the carbonyl group by the catalyst. This is

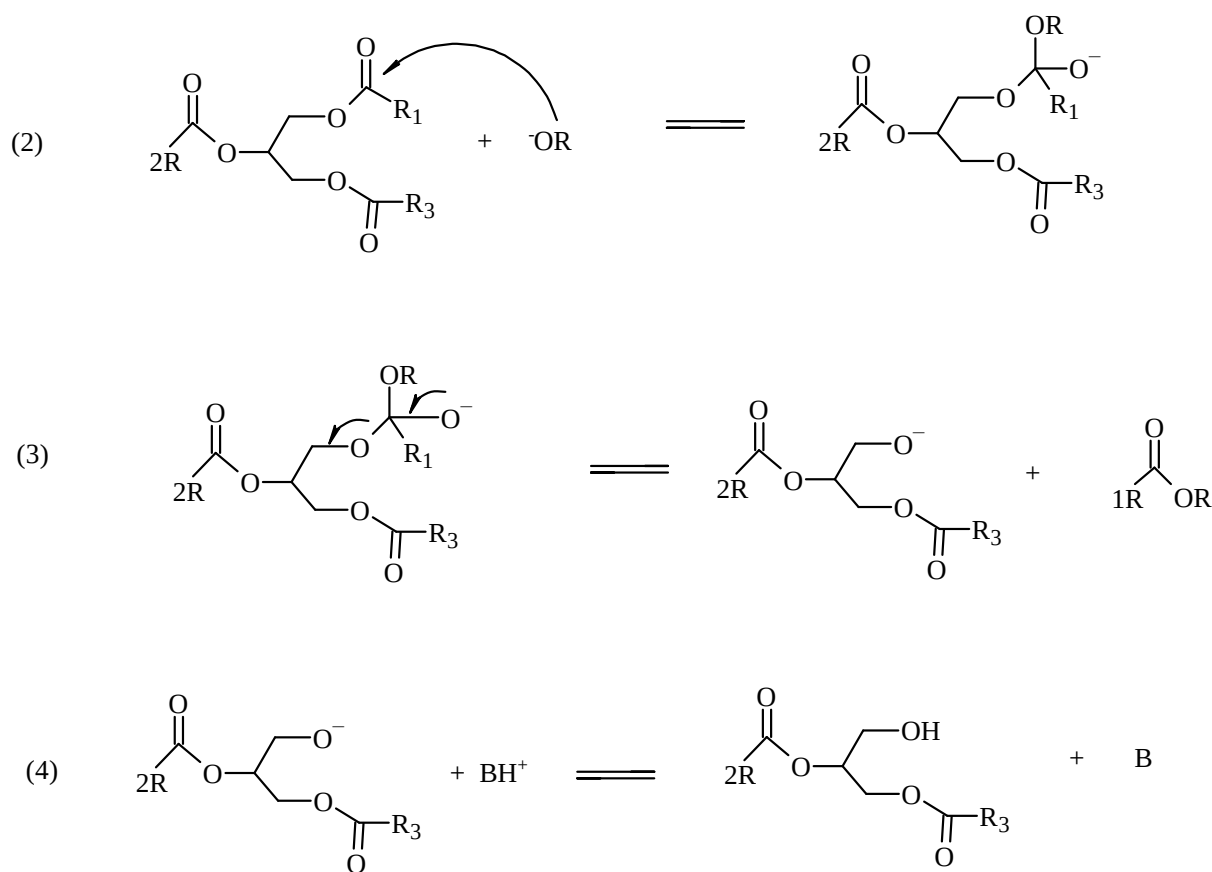
$$(1) \quad \text{ROH} + \text{B} \rightleftharpoons \text{RO}^- + \text{BH}^+$$


Figure 8: Mechanism for base catalyzed reaction[67]

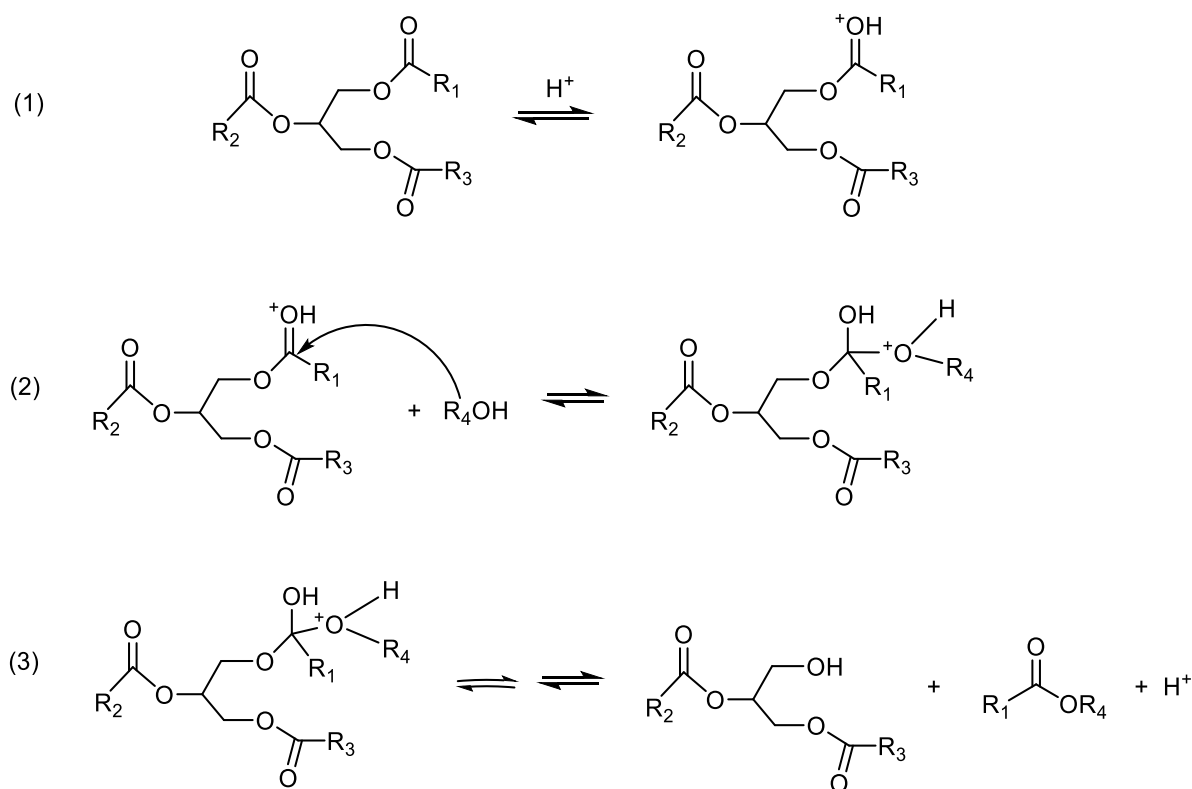


Figure 9: Acid catalyzed transesterification reaction [67].

1.3.1.3 Types of alcohols

The type of alcohol used in transesterification influences both the reaction kinetics and properties of the biodiesel that is formed[26]. When methanol is used the biodiesel formed is known as fatty acid methyl ester. The use of ethanol results in the formation of ethoxide ion as the active species which results in the formation of fatty acid ethyl ester and butanol results in fatty acid butyl ester. The solubilities of the alcohols in triglycerides also differ, shorter chained alcohols are insoluble while long chained alcohols are soluble. This affects the reaction kinetics of the alcoholysis. The reason for the difference in solubility is that polarity of alcohol decreases with increase in the hydrocarbon chain. Short chained methanol has the highest polarity, so it does not dissolve in triglycerides, and this slows down the reaction because of mass transfer limitations. The longer chained butanol creates a single phase with TG which makes the reaction faster[15,26]. When selecting an alcohol, consideration should also be given to the ease at which excess alcohol is removed and if its presence helps to improve the separation of glycerol at the end of transesterification. The use of long chained alcohols makes these two separation processes

difficult[26]. Methanol is the alcohol that is commonly used in transesterification because it is cheaper, and it is easier to separate excess methanol. Its use also simplifies the separation of biodiesel and glycerol.

1.3.2 Mass transfer limitations during transesterification

The transesterification reaction involves three main stages, being initial mixing or transfer stage, an irreversible chemical reaction stage and finally a reversible equilibrium stage[68–71]. The reaction is initially very slow because of the poor miscibility of methanol and triglycerides, which leads to mass transfer limitations. This stage is the rate limiting step. Several solutions have been suggested to overcome this problem. Stirring or agitation of reactants to improve mixing[72,73] is one of the solutions proposed. Studies have demonstrated that stirring plays very important role in the dispersion of methanol in the triglyceride hence speeding up the reaction[16,74] but it is an energy-consumptive process. Performing the reaction at higher temperatures can also help improve mass transfer, but it's energy-intensive and can lead to the loss of reactants such as methanol, which boils at a low temperature. Another solution is the use of cosolvent to create a single-phase system. The addition of a cosolvent has been found not only to reduce the time lag caused by mass transfer limitation but also in speeding up the separation of glycerol and biodiesel[15,57,75]. Solvents like tetrahydrofuran (THF) [15,76,77], 1,4-dioxane[78], dimethyl ether[76] and hexane[75] have been used as cosolvents for transesterification reaction.

1.3.3 Cold flow properties of biodiesel

Although fatty acid methyl esters have a lower viscosity than their fatty acid counterparts, their fatty acid compositions, specifically their aliphatic chains and oxygen positions, remain unchanged[79,80]. The presence of saturated FAMES affects how the biodiesel will behave in cold temperatures. FAMES begin to gel at low temperatures and become so thick that it cannot even be pumped into the fuel tank [81,82] resulting in poor flow properties. These poor flow properties affect engine performance and can result in high emissions of hydrocarbons, carbon monoxide and nitrogen oxides[81]. Cold flow properties of FAMES are usually evaluated via cloud point, cold filter plugging point and pour point. The cloud point is the temperature at which crystals and cloudy suspensions start appearing. This value appears much higher in biodiesel with a higher composition of saturated methyl esters like beef tallow methyl esters. The cold filter plugging point is the temperature at which the biodiesel forms crystals which then clog

the fuel filters. The pour point measures the lowest temperature at which the fuel flows. Poor cold flow properties are mainly caused by the high composition of saturated fatty acids present in biodiesel produced from animal fat. Table 1. 4 shows the cold flow properties of biodiesel produced from different feedstocks. The feedstock with the highest composition of saturated methyl esters has the worst cold flow properties.

Table 1. 4: Summary of saturated FAMES and values of Cloud points, pour points and Cold filter plugging points.

FAMES	%Comp of Saturated FAMES	Cloud Point (°C)	Cold Filter Plugging Point (°C)	Pour Point (°C)	References
Beef Tallow	57%	16.0	14	10	[42,83]
Chicken	32%	-5	3	-3	[32,38]
Lard	48%	4	5	5	[32,38]
Soybean	15%	2.3	-5.3	-2	[84]
Rape seed oil	13%	-3	-11	-9	[43,85]
Jathropa	21%	2	1	-7	[82]

There are several ways in which the poor cold flow properties can be improved. These include both physical and chemical methods. Physical methods include blending or mixing the FAMES with petroleum diesel. The disadvantage of this method is that there is still a high reliance on the fossil fuels[86]. Another method is thermal crystallization and fractionation, where the FAMES mixture is cooled and high melting point components are removed[87]. It is a labour and energy intensive process. Chemical modifications include converting to hydrocarbons by process such as hydrodeoxygenation, decarboxylation and decarbonylation.

1.3.4 Oxidative stability of biodiesel

Compared to fossil fuels, biodiesel is not stable in respect to long term storage. Biodiesel exists as mixture of saturated and unsaturated FAMES. It also has ester functional groups. Because of the presence of carbon double bonds and oxygen, it tends to oxidise over long periods of time[88,89]. The oxidation is made worse by factors such as exposure to light, air and increase in

temperature. When it oxidises biodiesel forms acids, aldehydes, ketones and insoluble sediments[89,90]. These new compounds change the fuel properties. Carboxylic acids increase acid value, which results in the corrosion of engine components, while insoluble sediments clogs filters. Consequently, if stored for extended periods of time, it may fail to meet regulatory standards such as the American Society for Testing and Materials (ASTM) and European standard (EN).

1.5 Current study problem

Biodiesel is an alternative source of energy which has capability of replacing quickly diminishing fossil fuels. It is produced by transesterification reaction in which excess methanol is reacted with triglycerides in the presence of a catalyst. Even though the reaction itself is simple, it is rather slow due to the poor miscibility of triglycerides with methanol. Cosolvents have been used to improve the miscibility of methanol with triglyceride. Use of cosolvents has been found not only to increase the speed of the reaction but also separation of biodiesel from glycerol by-product. In some cases, high products yields have been obtained at room temperature when cosolvents were used. The actual role of cosolvents in transesterification is clear, but understanding the properties of the best solvent is less clear. This needs to be investigated further.

Secondly, biodiesel has poor cold flow properties and poor oxidative stability. Poor cold flow properties make it hard to use the FAMES during winter months as it tends to form gels. This affects both the engine performance and durability. Poor oxidative stability is caused by the presence of double bonds and oxygen content in the FAMES. This makes it difficult for it to be stored for a longer period. The oxidation also produces compounds that affect the engine performance and its durability.

1.5.1 Aims

The aim of this work is to value the addition of biodiesel production and its usage. In the production aspect of the study, the aim is to understand how the addition of cosolvents accelerates the transesterification process. Regarding the usage part of the study, the aim is to improve both the cold flow features and oxidative stability by transforming biodiesel into green diesel.

1.5.2 Objectives

The objectives of the study are,

(1) To investigate how addition of cosolvents affects the interactions between triglyceride and methanol. The study seeks to interrogate the interaction of cosolvent around different sections of the triglyceride. The investigation seeks to accomplish the following:

- To investigate structural markers of good cosolvents
 - To investigate how the polarity of a cosolvent affects its interactions with triglycerides.
 - To investigate the effect of cosolvent on triglyceride conformation.
 - To investigate the effect of temperature on the interaction between cosolvent and triglyceride molecules.
- To investigate the use of thermodynamic properties as indicators of miscibility in triglycerides.

(2) To investigate at molecular level, nickel-molybdenum catalysed decarboxylation of biodiesel to produce green biodiesel to improve its cold flow properties and oxidative stability. Specific objectives include.

- Comparison of catalysed and non-catalysed reactions systems
- To investigate the effect of temperature on the decarboxylation
- To investigate the effect of different catalyst surfaces on the decarboxylation.

1.6 Thesis structure

The goal of this work is addressing two major drawbacks of biodiesel production processes, i.e., slow transesterification during production and poor cold flow and oxidative properties after production. To address these issues, the thesis will be divided into seven chapters. The next two chapters will give a survey of relevant literature and methodological approaches applied in addressing these issues including relevant theoretical methods.

Chapters 4 and 5 focus on application of cosolvents in overcoming the mass transfer limitations that are experienced in transesterification. Specifically, in Chapter 4, the emphasis is on binary interactions between cosolvent and triglyceride while Chapter 5 is on the ternary systems of triglyceride/cosolvent/TG/methanol.

The decarboxylation of FAMES as a way of improving the flow properties of biodiesel is reported in Chapter 6. Chapter 7 will give a conclusion of the findings as well as suggest future experiments.

CHAPTER 2

LITERATURE REVIEW

2.1 Reducing mass transfer limitations in biodiesel manufacturing

Mass transfer plays a very important role in the production of biodiesel. This is because oil and alcohol are immiscible. At the beginning of the transesterification there is poor mass transfer because of interface that exist between the immiscible oil and the methoxide catalyst layers [50]. As a result, the contact area between the two reactants is small. The contact area must be increased to increase the reaction rate, which can be accomplished by improving the miscibility of methanol in triglycerides. Increasing the temperature of the reaction mixture helps in improving the mutual solubilities of the two phases but increasing the temperature by 10 °C has been found to increase the solubility of methanol in oil by only 2–3 wt.%, and this leads to higher energy consumption[91]. There are two major ways apart from increasing temperature in which mass transfer limitation is reduced. These are addition of cosolvent and agitation/stirring.

2.1.1 Stirring or Agitation

Stirring or agitation is one of the main solutions to mass transfer limitations observed at the initial stages of transesterification. It involves stirring the reaction mixture with a magnetic stirrer or a propeller stirrer to create a homogenous mixture. This helps in improving contact area between methanol and oil. Agitating the reaction mixture at 500-1100 rpm increases the initial rate of transesterification of rapeseed oil, although it has no effect on the yield of biodiesel formed as demonstrated by Encinar et al. [53]. Stamenkovic et al. conducted a study on the effect of agitation speed on the methanolysis of sunflower oil. The aim was to investigate the impact of agitation intensity on the formation of FAME and the interfacial area. The study involved examining the mean drop diameter and drop size distribution at different agitation speeds in a batch stirred reactor in systems with and without the transesterification reaction. The results showed that as the agitation speed increased, the drop size distribution became narrower and the interfacial area increased, leading to an improved reaction rate at the interface[92].

Roy et al.[72] used mathematical model to study the effects of stirring on the mass transfer limitations in the production of biodiesel from *Jatropha curcas* oil and methanol. From their findings they concluded that indeed increasing the speed of stirring helps reduce the reaction

time lag that is observed at the initial stages of transesterification, **Error! Reference source not found.**

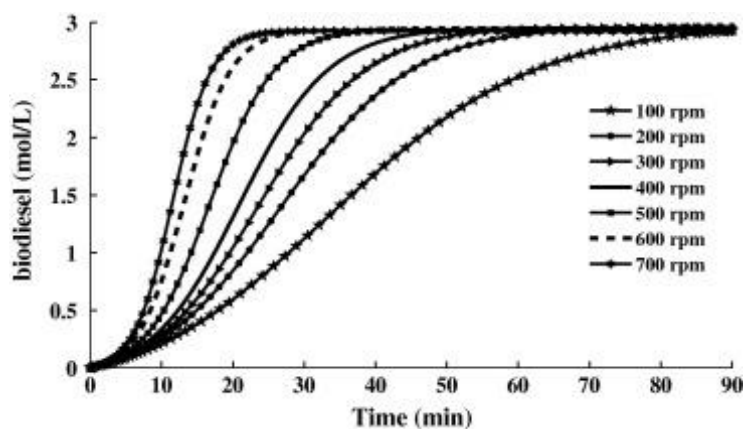


Figure 10: Effect of stirring speed [72]

In the transesterification of beef tallow, Ma et al.[93], investigated if mixing had an effect on the reaction. They first added NaOH-methanol mixture to melted beef tallow and nothing happened. When they repeated the reaction with stirring products started appearing. They concluded that mass limitation that is caused by immiscibility improved with stirring. Just like with Encinar et al.[53] they found out that stirring had no effect on the yield of FAMES formed. Nahas et al.[94] studied the effect of stirring in the production biodiesel from sunflower oil and waste cooking oil. The alcohol used was methanol and the reaction was catalysed by a heterogenous catalyst derived from scallop seashells. They found out that increasing stirring rate from 400 to 700rpm increased the yield of biodiesel obtained from 35% to 60%. Agitation of the reactants helped in overcoming the mass transfer limitations between methanol, oil and a catalyst.

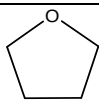
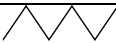
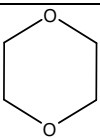
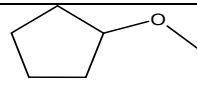
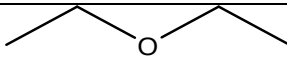
Even though the stirring is essential in helping reduce the mass transfer limitations, it has the disadvantage of being an energy-consumptive process[93]. It leads to an increase in the production cost hence an increase in the final price of biodiesel. There is a need to find a more energy efficient solution, hence the recent interest in using cosolvent.

2.1.2 Use of cosolvents

A cosolvent, is a liquid that is soluble in both liquid reactants and is added in small quantities to the reaction mixture to improve the solubility between two liquids, which on their own are immiscible or poorly miscible[95]. For a solvent to be considered a cosolvent for

transesterification it must have high solubility in both triglyceride and methanol and should not react with either. Methanol is highly polar while triglyceride has both polar (ester heads) and non-polar (hydrocarbon chains). An ideal cosolvent should be able to interact strongly with the polar and non-polar parts of both methanol and triglyceride to help reduce self-interaction of each component which ends up inducing phase separation. The other thing to look for when selecting a cosolvent is boiling point. This is because it should be easy to remove the cosolvent at the end of the transesterification so that it does not affect the quality of the biodiesel produced and increase the production costs. Most of the cosolvents currently used have boiling points that are closer to methanol. This enables it to be removed with excess methanol at the end of reaction. The cosolvents should also be miscible in glycerol, this has been found to help in speeding up the separation of the products at the end of transesterification. The addition of cosolvent is expected to lead to low reaction times, faster reaction rates and lower reaction temperatures[96]. Listed in Table 2. 1 are physical properties of some common transesterification solvents. Below we review these solvents and their usage.

Table 2. 1: Physical Properties of cosolvents

Physical properties	THF	Hexane	1,4-Dioxane	CPME	DEE
Structure					
Density (g ml ⁻¹)	0.8876	0.6606	1.033	0.8630	0.7134
Boiling Point	66	69	101.1	106	34.6
Flash Point (°C)	-14	-26	12	-1	-9
Dipole moment	1.7	0.08	0.45	1.27	1.15
Dielectric constant	7.4	1.89	2.25	4.76	4.34

2.1.2.1 Tetrahydrofuran (THF)

Tetrahydrofuran is an organic compound with a molecular formula of C_4H_8O . It belongs to the ether homologous group and is heterocyclic in nature. It can be produced from renewable resources like biomass during catalytic hydrogenation of furan. It is nontoxic, unreactive, and relatively cheap when compared to other solvents. It has many uses including being a solvent and in the production of a polymer known as poly tetrahydrofuran or poly (tetramethylene ether) glycol. It is slightly polar which enables it to dissolve both polar and nonpolar compounds. These properties have made it a good candidate to be used as a cosolvent to improve mutual solubilities of oil and methanol in transesterification reaction. Table 2. 2 summarizes some of the investigations in which THF was used as a cosolvent. Encinar et al.[53] investigated the effect of addition of THF and other solvents including acetone, diethyl ether (DEE),dibutyl ether, tert-butyl methyl ether(t-BME) and diisopropyl ether (ddPE) in the transesterification of rapeseed oil. They selected these solvents because they had both polar and non-polar parts in their structures. The study found that THF, DEE, and t-BME were the most effective in enhancing the mass transfer limitations, which ultimately resulted in a reduction of the reaction time. The addition of THF also accelerated the separation of glycerol and biodiesel. Additionally, THF was utilized as a co-solvent in the transesterification of palm kernel oil and methanol under supercritical conditions[75]. Sawangkew et al, selected cosolvents based on how close their boiling points were to methanol, which made it easier to recover them at the end of the reaction. THF proved to be a good cosolvent even under supercritical conditions. Their findings also showed that addition of cosolvent did not have any effect on the yield of biodiesel produced.

When preparing biodiesel from soybean oil, Boocock [97] added THF to a mixture of methanol and soybean oil to create a one phase system. The one phase system speeded the reaction even at room temperature. Stirring was also not necessary, which helped in reducing the production cost. The addition of THF also simplified the separation of glycerol and biodiesel, in fact it was 5 times faster than it was in the mixture without THF. Aghel et al. [98] also investigated the effect of cosolvent in transesterification of waste cooking oil using kettle limescale as a catalyst. Using THF as a cosolvent helped in achieving the yield of 95.2% biodiesel in 10 mins.

Table 2. 2: Summary on the use THF as a cosolvent in production of biodiesel.

OIL	Catalyst	Time (mins)	Temp (C)	% Yield	Reference
Waste cooking	Kettle limescale	10	65	95%	[98]
Soybean	NaOH and NaOCH ₃	10	rtp	90%	[97]
Rapeseed	KOH	120	30	95-97%	[53]
Palm Kennel	-	30	350	95%	[75]
Waste vegetable oil	NaOH	-	70	95%	[57]
Soybean and Coconut	NaOH	7	23	90	[15]
Soybean	NaOCH ₃	480	70	-	[99]
Rubber seed oil	KOH	30	52	97%	[100]
Canola	H ₂ SO ₄	24	20	90	[101]

2.1.2.2 Diethyl ether

Diethyl ether (DEE) is one of the commonly used ethers as cosolvent in the transesterification reaction. Just like THF it has been found to reduce the mass limitations that are experienced at the beginning of the reaction. It is also an aprotic solvent. It is used mainly in the non-polar liquid-liquid extraction and as an organic solvent. It is also used as a fuel and has a high cetane number. These properties make it an ideal candidate for use as a co-solvent. Encinar et al. [53] used DEE as a cosolvent in the production of FAMES from rapeseed oil. They were able to achieve high yields of 98% under a short reaction times of 30 mins and low temperature of 30 °C. Lian et al.[102] also found that the use of DEE produced high yields of 98% at very low temperatures even room temperature (Figure 11). Separation of FAMES from glycerol was also easier and faster when DEE was used as cosolvent.

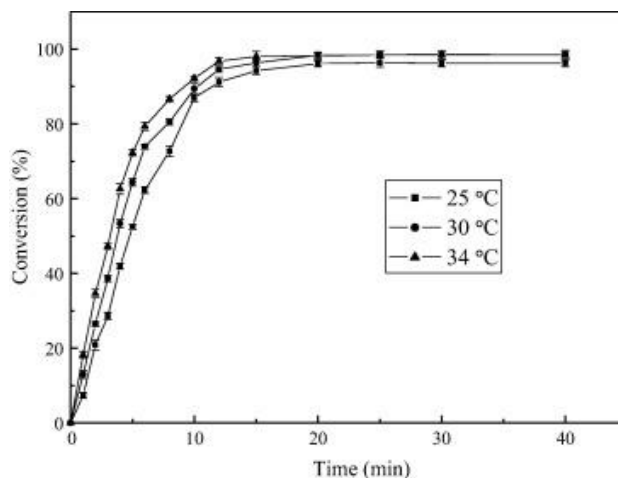


Figure 11: Percentage conversion achieved in the transesterification of soybean oil using DEE as cosolvent at low temperatures[102].

2.5.2.3 Cyclo pentyl methyl ether (CPME)

Cyclo pentyl methyl ether also known as methoxy cyclopentane (CPME) is a member of the ether functional group of organic compounds. It is heterocyclic in nature with a molecular formula $C_6H_{12}O$. It has a higher boiling point of 106 °C when compared to other ethers. Its solubility in water is lower than that of THF. It is stable in both acidic and basic conditions and is not prone to ring opening in acidic medium like THF[78,103]. Unlike other ethers which rapidly form peroxides when exposed to air, formation of peroxides in CPME is very slow[104]. Its stability, hydrophobicity and how easily it dries after being in contact with water has made CPME to be very promising as a solvent, and in fact has been used as a solvent in many organic synthetic process[103,105]. It has been used as a solvent for oil extraction and in the purification of biodiesel. Jesus et al., [106] used CPME together with 2-methyltetrahydrofuran (2-MeTHF) as cosolvents in the synthesis of biodiesel from microalgae. It was also used in purification of the FAMES produced. Figure 12 shows that using CPME as a cosolvent produced high yields of biodiesel which were also of very high purity.

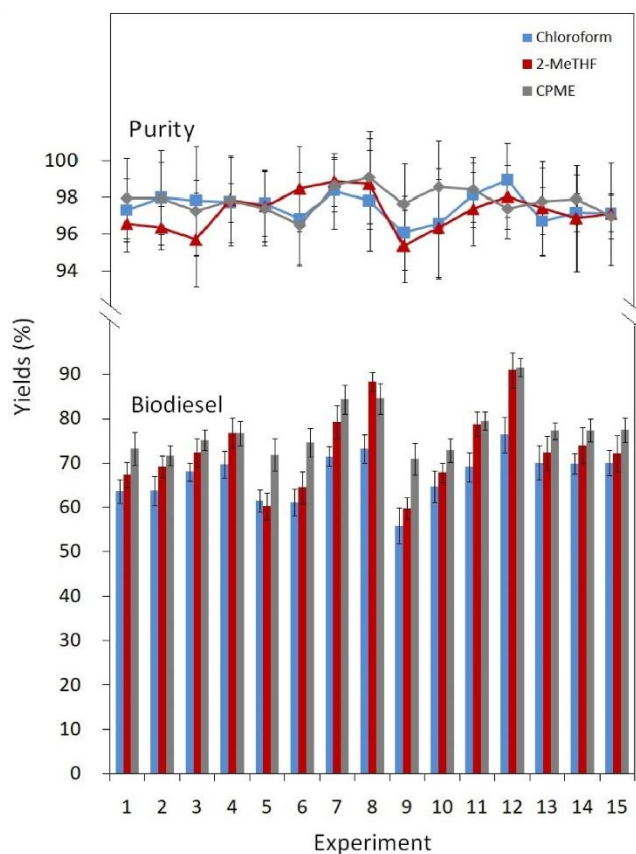


Figure 12: The percentage yield and purity of biodiesel produced using CPME as a cosolvent[106].

2.1.2.4 Dioxane

1,4-Dioxane is also from the ether homologous group. It is a colorless liquid with a boiling point of 101°C[107]. The dioxane molecule is flexible, taking on two forms: chair and boat conformations. It is a versatile aprotic solvent with a wide range of applications, including use in the dissolution of inks and adhesives. Because of its lower toxicity and higher boiling point, it is sometimes used in place of tetrahydrofuran (THF) in certain processes. There are several reported cases where dioxane was used as a cosolvent in transesterification reactions. Boocock's et al., used dioxane in the fast one phase transesterification of soybean oil. The selection was based on its ability to dissolve both methanol and triglycerides. Dioxane was also used as a cosolvent in the CaO catalyzed transesterification of sunflower oil. Upon addition to the reactants, a single-phase system was formed, resulting in a 94.8% yield of biodiesel produced[108].

2.1.2.5 Hexane

Hexane is a hydrocarbon and a member of the alkane homologous series. Apart from being a non-polar solvent, it is already being used as a fuel. Its ability to dissolve triglycerides and having a boiling point that is closer to methanol makes it a good candidate for use as a cosolvent. Hexane was used as a cosolvent in the methanolysis of poultry fat using Mg-Al hydrotalcite derived catalysts by Liu et al. [109]. Their results show that at early stages, the presence of hexane as a cosolvent speeds up the reaction. Its hydrophobicity enabled it to interact strongly with the triglyceride than with methanol. Its addition to reaction mixture containing methanol and triglyceride, it made triglyceride molecule to change from tuning fork conformation which is rigid to a less rigid conformer proposed [110]. This change helped in improving the interactions between methanol and TG. However, as the reaction progressed, biodiesel and glycerol which are more polar were formed which slowed the reaction. Hexane was also used to create single phase in the transesterification of camelina oil and ethanol[111]. Its addition increased the yield of biodiesel formed from the 44% to 66% in a 20-minute period. Sawangkew et al. found out that addition of hexane helped in speeding up the reaction, 95% biodiesel was formed in 10 minutes. Another advantage of using hexane as a cosolvent is that it helped in reducing soap formation[112].

2.1.3 Theoretical studies on the use of cosolvents

From the above literature reviews, it is clear that cosolvents reduce the mass transfer limitations that are experienced during the transesterification reactions. It is important to understand the role of these cosolvents and how they improve the miscibility of methanol in triglycerides at molecular level. To the best of our knowledge, very few theoretical and computational studies have been conducted to understand how cosolvents improve the miscibility of methanol with triglycerides.

However, research has been conducted on cosolvency in other systems. Mohan et al. [113] investigated the effects of adding cosolvent dimethyl sulfoxide (DMSO) to improve the solubility of glucose in ionic liquids (ILs) using molecular dynamics simulations. They used NAMD 2.10 software and Amber force field for the molecular dynamic's studies. The interaction energies were calculated by summing up non-bonded electrostatic and van der Waals energies obtained from molecular dynamics trajectories. The results showed that addition of cosolvent resulted in stronger interaction energies showing improvement in the solubility of

glucose in ILs. The radial distribution functions (RDF), spatial distribution functions (SDF) and number of hydrogen bonds were also used to quantify mixing and they all showed that the addition of DMSO to ILs, weakened the interactions between anion and cation of ILs, which helped in enhancing the solvation of glucose.

In another study, molecular dynamics simulation was used to study the effect of 2,2,2-trifluoroethanol (TFE) in stabilizing peptides in water. Using GROMACS software and GROMOS96 force fields, the distributions of cosolvent around the peptides were investigated and the results showed that in TFE-water mixture, the organic cosolvent aggregated around the peptide forming a matrix which promoted the formation of an ordered secondary peptide structure. Removing water from the surface of TFE removed hydrogen-bonding and provided a low dielectric environment which in turn favored the formation of intrapeptide hydrogen bonds. It was also shown that TFE interacted only weakly with nonpolar residues, which meant it was not able to severely disrupt hydrophobic interactions within the peptides. Therefore, the addition of TFE as a cosolvent promoted stability of peptides.

Effect of solvents (butyl acetate, isobutyl methyl ketone, ethyl acetate, tetrahydrofuran, and dichloromethane) on the dynamic properties of polymethacrylate (a-PMMA) were studied using COMPASS force field by Tung et al. [114]. The dynamic properties of the solutions as mean-square end-to-end distance $\langle R^2 \rangle$ and mean square radius of gyration $\langle S^2 \rangle$ were analyzed. The results showed that R^2 increased with the dipole moment of the surrounding solvent systems. The RDFs of H-H atomic pairs were also calculated and showed that the expansion of the polymer chains was dependent on the conformation of solvent molecules not the interaction between solvent and polymers. Additionally, in the calculations of non-bonded interaction energy, in all the binary pairs, the Coulombic forces were predominant when compared to van der Waals in the polymer-solvent interactions.

Paul et al. conducted a study to investigate the stability and solvation structure of psilocybin in water and 35 different organic solvents using molecular dynamics and DFT calculations[115]. Their research revealed that the process of solvation was mainly governed by hydrogen bonding between psilocybin and the solvent. The results of the free energy of solvation showed that psilocybin was more soluble in water as compared to organic solvents. Additionally, the radial distribution functions were utilized to measure the strength of interactions between psilocybin and solvents based on their intensity and distance.

Structural properties of the solvation of anthracene in water-saturated tricaprylin was investigated using the molecular dynamics and ab initio calculations[116]. The authors used Amber 8 force field and HF/6-31G*. The scaled free energy of transfer was found to be similar to experimental results. The radial distribution function for tricaprylin's central carbon atom, with the neighboring tricaprylin molecules suggested local organization. The existence of conformational preferences for individual tricaprylin was also investigated with results indicating that each of the two outer aliphatic chains of tricaprylin were positioned between 50° and 100° from the middle chain, with nothing near 0°, due to steric hindrance. The results also showed that approximately 50% of the dissolved water existed as monomers, while the other 50% existed as self-associate.

Regarding the thermodynamic properties of mixings, various models are currently employed to describe the phase behaviours of liquid mixtures at the phase boundary. The commonly used theoretical models include Universal Functional Activity Coefficient (UNIFAC), Non-Random Two Liquid model (NRTL), ab initio calculations and Flory-Huggins theory.

Group contribution methods like the UNIQUAC and UNIFAC models are used to estimate activity coefficients of components based on their functional groups. Behavior and properties of ternary mixtures comprising methanol/biodiesel/glycerol and methanol/water/biodiesel were predicted using several versions of the UNIFAC model[117]. The original UNIFAC and Dortmund-UNIFAC models were found to better predict binary systems containing methanol/soybean biodiesel and methanol/glycerol systems. The original UNIFAC model, along with the LLE-UNIFAC model, was found to offer a more accurate representation of the methanol/methyl oleate/glycerin and methanol/water/rapeseed biodiesel systems. However, all the UNIFAC models presented were found to overestimate the distribution coefficients of methanol which tended to underestimate the amount of methanol which was dissolved in biodiesel. In another study, the effect of cosolvents (THF, acetone, and hexane) on the enzyme-catalyzed transesterification of triolein was investigated using LLE-UNIFAC and experiments[118]. The addition of cosolvents (acetone and THF) was found to prevent enzyme aggregation which in turn helped enhance reaction rates. The addition of hexane inhibited the activity of enzymes, resulting in low yields of biodiesel produced. Researchers utilized free energies and activities calculated through the UNIFAC model to investigate why hexane

produced slower reactions compared to acetone and THF. It was discovered that methanol and glycerin had the lowest transfer energies from the bulk to the water layer in the presence of hexane. Superfast transesterification of triolein to produce biodiesel was carried out in the presence of cosolvents THF and liquified dimethyl ether by Hidetoshi and coworkers. The researchers preliminarily utilized the LLE-UNIFAC model to predict the compositions of triolein, methanol and cosolvents that will result in the formation of a single phase. The entire transesterification process was completed in just three minutes using the calculated compositions[119]. However, the LLE-UNIFAC model's limitation was its inability to predict exactly when glycerol was formed because its formation resulted in a biphasic system, which slowed down the reaction. The phase behavior of ternary systems of biodiesel/methanol/glycerol and methyl palmitate/methanol/glycerol was also investigated using the UNIQUAC and NRTL thermodynamic models. The obtained results demonstrated good correlation between the models and experimental data for predicted tie lines[120].

Computer simulations can be used to predict the solubility of substances in triglycerides by analyzing their structural, dynamic, and thermodynamic properties. However, the current research on the use of cosolvents has highlighted several issues with the studies that have been conducted. Experimental studies have assumed that adding cosolvent results in the formation of a single phase, which helps to speed up the process, but they lack information on the point at which the mixture becomes a single phase. Molecular dynamics simulations can provide this information at molecular level. Fewer studies have focused on the molecular level studies of oil/methanol/cosolvent systems, and even the thermodynamic models that have been reported have mainly focused on biodiesel/methanol/glycerol systems, with little consideration given to systems that include cosolvents.

This study seeks to understand the major interactions involved in the formation of a single phase of triglyceride/methanol/cosolvent systems. Studying these is the first step to a molecular level approach to designing alternative solvents that could be greener and cheaper. The problem will be addressed in two parts, with the first focusing on the interactions between cosolvent and triglycerides. This will be discussed in Chapter 4 of this thesis. Information gathered here will help in the screening of potential cosolvents. On the second part, ternary mixtures of methanol/oil/cosolvents will be investigated via application of the Flory-Huggins solution theory

which has been used to study solubility of polymers. Chapter 5 will focus on the ternary methanol/oil/cosolvent mixtures.

2.2 Improving flow properties and oxidative stabilities of biodiesel

Biodiesel is more polar than diesel fuel, due to the presence of electronegative oxygen. This makes biodiesel more viscous than diesel fuel. Viscosity plays a critical role in determining performance and usability of the fuel. The recommended viscosity range for biodiesel is 1.9-6.0 mm²/s as per American Standard Testing Materials (ASTM). Low viscosity biodiesel can lead to leakages and increased wear and tear on engine components. On the other hand, high viscosity may lead to the injection pump being unable to supply enough fuel to fill the pumping chamber. In general, fuels that are used for compression ignition engines can cause starting problems when exposed to low temperatures. This is because the flow properties tend to deteriorate, which results in the formation of small crystals that get suspended in the liquid phase. These crystals can partially or completely clog fuel filters, reducing the flow section through the pipes. Furthermore, they tend to settle on the inner walls of the fuel system's pipes, causing poor engine fueling and loss. There are two major ways in which oxidative stability and flow properties can be improved, i.e., blending and conversion to green diesel. These will be briefly discussed in subsections that follow.

2.2.1 Blending

Blending is the process of mixing traditional fossil fuels with biodiesel. This technique is commonly used to address issues with the physical properties of the fuel, such as high flow properties (like viscosity, cloud point, pour point, and cold filter plug point) that can have negative effects on the engine[121]. One of the most significant advantages of biodiesel is that it can be blended with diesel fuel in any proportion without any need for engine modification. A study conducted by Canakci focused on the combustion and emission properties of blends of soybean oil methyl ester and diesel[41]. They found that addition of soybean oil biodiesel to fossil diesel significantly reduced the unburned hydrocarbon, carbon monoxide, and particulate matter emissions compared to pure diesel fuel. However, NO_x emissions increased by 11.2% compared to diesel fuel. These findings were confirmed by Mofijur et al., when using Jatropha biodiesel as a blend for petroleum diesel. In addition to emissions, the investigation included the physico-chemical properties of Jatropha biodiesel and its blends[122,123]. The findings indicated that the viscosity of B10 (10% biodiesel and 90% petroleum diesel) and B20 were

similar to diesel. The oxidation stability of the two blends also met European standards. When blends were used on a single-cylinder diesel engine, the engine's performance was comparable to that of diesel fuel. One of the main drawbacks of blending biodiesel with petroleum diesel is that the reliance on petroleum diesel, which is depleting rapidly, remains high. However, converting biodiesel to green diesel can reduce this dependence, especially because the resulting diesel is similar to fossil diesel.

2.2.2 Conversion to green diesel

The conversion of biodiesel to green diesel can also improve its cold flow properties and oxidative stability. This can be achieved by decarboxylating the ester part that is responsible for poor oxidative stability, high acidity, and poor flow properties. The produced fuels are known as green or renewable diesel and is superior to both biodiesel and fossil diesel in terms of performance and reduced emissions[124] and can be readily used in the transportation industries without any modification to current engines. There are three major ways in which this can be achieved being decarboxylation, hydrodeoxygenation and decarbonylation. All these three reactions are endothermic and require the use of catalysts to lower the activation energies and reduce the temperature of the reactions. Presented in Figure 13 is a scheme which shows the differences between the three reactions. All the three reactions may occur simultaneously, but the path taken is influenced by the reaction conditions i.e., partial pressure of hydrogen, temperature and catalysts used. Both saturated and unsaturated FAMES can be deoxygenated to yield olefins and alkanes with high conversion and selectivity. The catalysts are always used to lower the activation energy and make the reactions economically feasible.

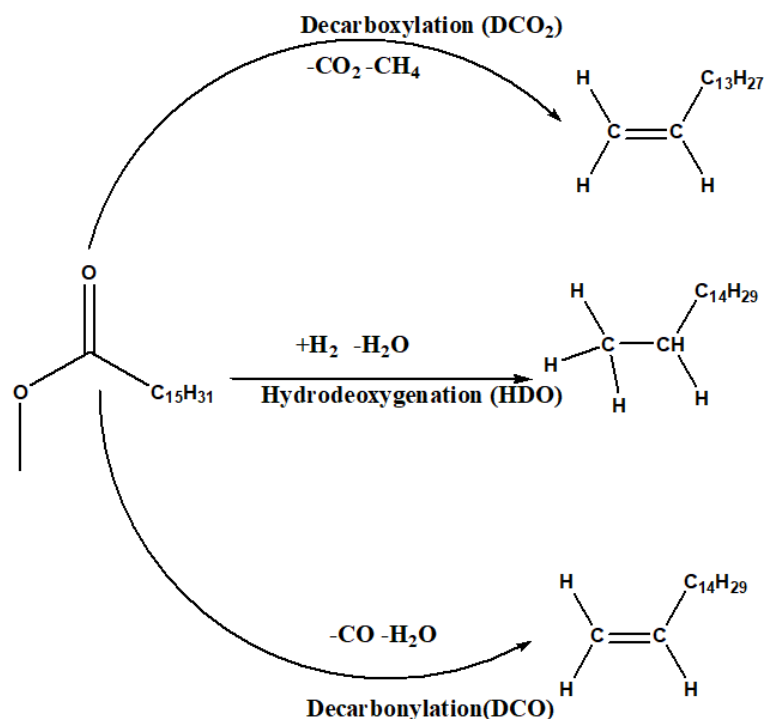


Figure 13: Decarboxylation, decarbonylation and hydrodeoxygenation of methyl palmitate [125].

2.2.2.1 Hydrodeoxygenation (HDO)

Hydrodeoxygenation (HDO) is one of the ways in which FAMES are converted to hydrocarbons by the cleavage of ester in the molecule. The reaction requires pressurised hydrogen and a catalyst. The alkane that is produced has the same number of carbons as the feed stock which can either be fatty acids or FAMES, and the oxygen is removed as water. The conversion of FAME (methyl stearate) to HCs using HDO reaction was investigated by Chen et al.[126]. The catalyst used in their investigation was a bifunctional Ru/HZSM-5. They were able to achieve high conversions of 99.1% of methyl stearate and the main products were heptadecane and octadecane at selectivity of 40.6 and 38% respectively. HDO of biodiesel using nickel and copper catalyst which were supported on CeO₂-ZrO₂ was investigated by Dundich et al.[127]. They were able to produce alkane heptadecane at a high selectivity of 80% under very mild conditions of 1.0 MPa hydrogen pressure at 290 °C. Senol et al.[128] used Ni-Mo/Al₂O₃ and Co-Mo/Al₂O₃ to study the HDO of methyl heptanoate. Their results showed that Ni-Mo/Al₂O₃ catalyst was more effective at the production of hydrocarbons than the Co-Mo/Al₂O₃ catalyst. The main products for the reaction were heptane at selectivity of 44% and hexane at a selectivity of (33%) while products

formed in small quantities included alkenes and acids i.e., heptene, hexene and heptanoic acid. The method used showed preference toward the formation of saturated hydrocarbons than unsaturated hydrocarbons. FAMES produced from transesterification of rapeseed oil was converted to hydrocarbons by Yakovlev et al. using HDO process[129]. The catalysts used in the HDO were a mixture of Cu-Ni supported on $\text{ZrO}_2/\text{CeO}_2$. The results showed 100% conversion of FAMES with 75% selectivity towards formation of heptadecane ($\text{C}_{17}\text{H}_{36}$).

Hexadecane was produced by HDO of methyl palmitate over Ni/desilicated meso-Y catalyst and the selectivity of the target product was 64.8%[130]. To confirm the mechanism for the HDO reaction the density function theory (DFT) calculations were carried out and the energies needed for the cleavage of ester group were calculated. The enthalpy change required to produce pentadecane was -130.2 kJ/mol via HDO pathway and this was lower than -68.6 kJ/mol needed to produce hexadecane by decarboxylation. Tan et al. , used quantum mechanical calculations and experimental methods to study the HDO of anisole on Pt, Ru, and Fe catalytic surfaces[131]. From their DFT calculations results they were able to deduce the mechanism of HDO on various metals surfaces reactions and were able to explain how different metal catalysts influence the reaction pathways. Jin et al. [132] used combination of DFT and Reactive Force Field (ReaxFF) to investigate HDO of furfural in supercritical water. Using these two techniques and products formed they were able to propose the mechanism for the HDO reaction. HDO of biomass on Pd surfaces was also investigated by Mark et al. [133] who used several theoretical techniques including QM/MM and DFT calculations. According to the results obtained on the HDO of furans and benzylic alcohols, the rate determining step involved the transfer of hydrogen atoms adsorbed on the Pd surface to hydroxyl groups in the alcohol reactants. The mechanisms proposed were able to explain experimental findings obtained by other researchers.

The disadvantage of HDO is that it requires excess pressurized hydrogen gas to take place, and this makes it expensive. The pressurized hydrogen gas needs specialized reaction vessels for the reaction to be safe, further increasing the cost of production. The yield of the alkanes produced is also low.

2.2.2.2 Decarboxylation and Decarbonylation

Another way of converting FAMES to hydrocarbons is by decarboxylation or decarbonylation (deCO_x). The two differ in the production of side products. In decarboxylation, carboxyl group is

removed from the molecule (organic acid or FAMES) as CO₂ while in decarbonylation it is removed as CO and H₂O molecules. These routes cannot be easily distinguished from each other due to the easy reaction of CO₂, CO and hydrogen on the surface of the catalyst[134]. Both reactions can proceed in the presence or absence of hydrogen and if it is present, it is always of lower partial pressures when compared to requirement in HDO. The decarboxylation is rather interesting because it is cheaper and energy efficient when compared to HDO. When performed on a methyl ester, deCO_x results in CO₂, CH₄ and a long straight hydrocarbon chain which is one carbon less than the original FAME[135]. Like HDO, deCO_x requires high temperature and catalyst to take place.

Investigations of the conversion of FAMES to HCs using various theoretical techniques have been reported. These investigations include both catalyzed and non-catalyzed reactions. Computational calculations give an insight to the processes and mechanistic behaviors of both substrates and catalysts at atomic/molecular level. Information gathered is useful in optimizing catalyst design and preparation. Computational simulations have proven to be the most useful tool to complement experimental findings. Summarized below are some of the computational based studies on decarboxylation.

Molecular dynamics studies of the decarboxylation of tripalmitin[136] and trilinolenin[137] using reactive force field (ReaxFF) was carried out at temperature ranging from 1500 and 2500 K by Zhang and co-workers. Their results show that although the triglycerides were different structurally their decomposition route was almost identical. The reaction was initiated by ester linkage cleavage resulting in the formation of one C₃H₅[•] radicals and three straight chain C₁₆H₃₁O₂[•] radicals in case of tripalmitin and C₁₈H₂₉O₂[•] in trilinolenin. This is then followed by the decarboxylation of the oxygenated radical to form C₁₅H₃₁[•] and C₁₇H₂₉[•] radicals. The hydrocarbon radicals are then rearranged to form different alkane, alkenes and aromatics. It was also found that temperature had an effect in the number of alkanes and alkenes formed. These results are similar to those reported by Zhang et.al,[138] who also used ReaxFF to study the pyrolysis of triolein. The summary of their mechanism of the pyrolysis is presented in Figure 14. The proposed mechanism also begins with the breakage of C-O bonds to form CH₃[•] and C₁₈H₃₃O₂[•] radicals. The main products reported here are still ethene and carbon dioxide. In another study, the mechanism for the decarboxylation of lauric acid to hydrocarbons using non-heme iron oxidase catalysts was proposed based on quantum mechanics/molecular mechanics

(QM/MM) calculations. For the quantum mechanics part hybrid density functionals UB3LYP combined with the basis sets 6-31(d, p) was used while DL-POLY was used for molecular mechanics' part. From their results Zhang et al.[139] deduced that the decarboxylation was initiated by $\text{Fe}^{\text{III}}\text{-OO}^{\bullet-}$ complex. For this to happen lauric acid should be coordinated to the Fe center and this facilitated the β -H abstraction which initiated the decarboxylation. The catalyst free deoxygenation of fatty acid (palm olein) was carried by the same authors, again using ReaxFF[140]. The effect of moisture content and temperature were also investigated. At high temperatures the main products of palm olein deoxygenation were C_2H_4 and CO_2 and these were also formed at faster rate. The increase in moisture in the system also had a positive effect in the generation of products and resulted in the faster formation of CO_2 and CH_4 . These results of the simulation agreed with experimental findings[141].

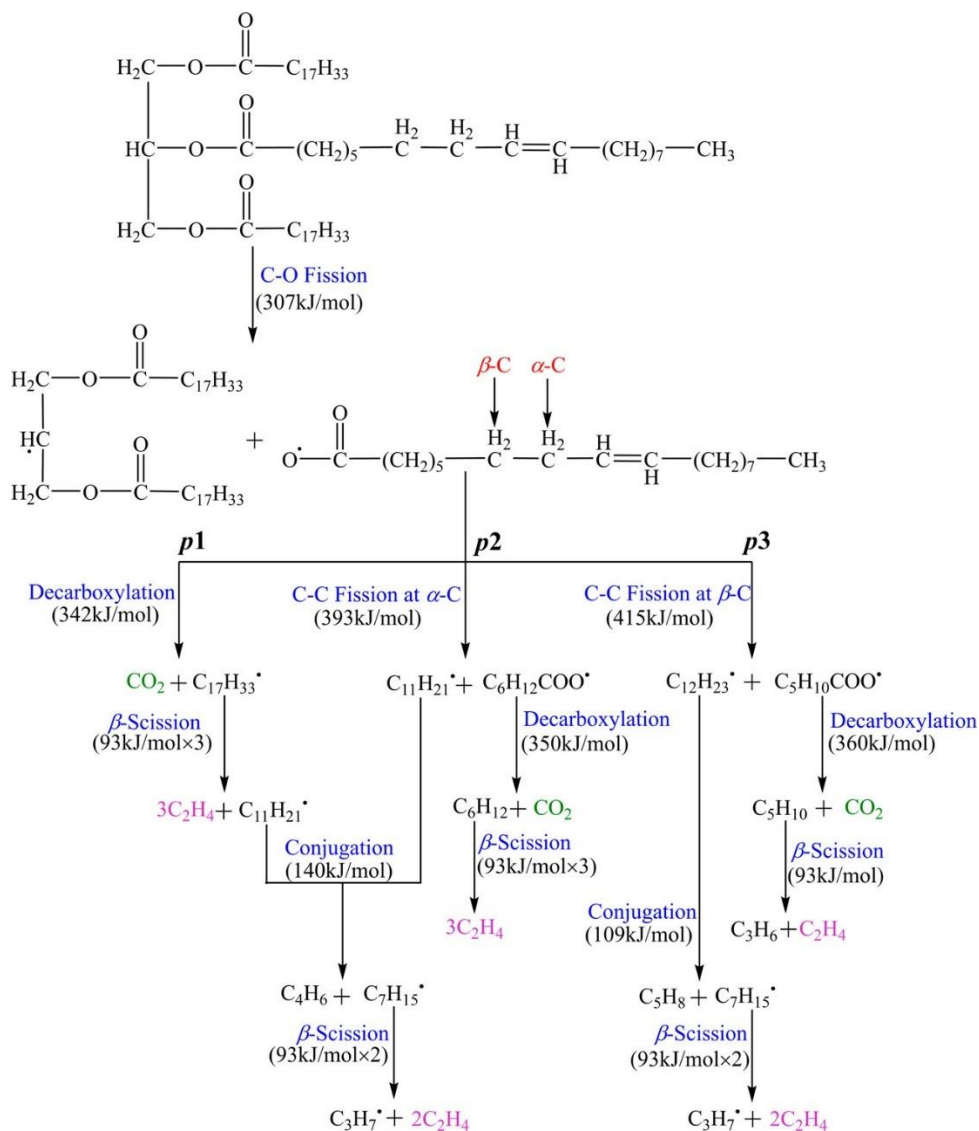


Figure 14: The decomposition reactions of triolein[138].

Even though there are many reports on catalyst-free decarboxylation (pyrolysis), there are few reports on theoretical studies of catalyzed decarboxylation. Pyrolysis requires a high temperature to occur. This can be remedied by using a catalyst. A mixed metal catalyst Nickel Molybdate is one of the promising catalysts for decarboxylation of FAMES.

2.2.2.3 Catalysts for the conversion of biodiesel to green diesel

The primary catalysts for the deCOx are the noble metals Platinum(Pt) and Palladium(Pd)[142–144]. These catalysts are very expensive. The emphasis is now on lower-cost transition metals such as nickel and molybdenum. When these are alloyed or are supported in materials like C,

Al_2O_3 , zeolite, high yields and activity towards the production of hydrocarbons are observed that are comparable to using noble metals[127]. The use of sulphided Ni-Mo catalyst have also been reported in deCOx reactions, however addition of sulphur resulted in production of sulphur dioxide which is an air pollutant. Snare and co-workers[145–147] have reported the decarboxylation/decarbonylation of methyl esters and fatty acids to hydrocarbons. Stearic acid, methyl oleate, oleic acid, and linoleic acid were used as substrates. Catalysts of Pd, Pt, Ru, Mo, Ni, Rh, Ir and Os that were supported in oxides of metals or carbon were screened. The findings indicated that Pd and Pt catalysts performed better when compared to others in terms of both activity and selectivity towards the desired hydrocarbons. Conversion of methyl stearate to hydrocarbon, heptadecane using supported Pd catalysts was reported by Han et al.[142], with Pd metal supported in BaSO_4 yielding the best results when compared to other catalysts. Pd/ BaSO_4 showed conversions of greater than 99% and selectivity of greater than 98%. The study was extended to esters like methyl palmitate, ethyl stearate and ethyl octanoate where high selectivity and high conversions were still observed. The decarboxylation of stearic acid, ethyl stearate, and tristearine using metal catalysts that were supported on carbon to form hydrocarbons was also reported by Murzin et al.[148]. The results showed that all the three compounds resulted in production of *n*-heptadecane as the main product with high selectivity.

Metal oxides have been widely used as catalysts for conversion of esters to hydrocarbons[149–151]. Mixed metal oxides have been found to have more active basic sites and acidic sites which increases their surface area, which in turn reduces reaction time and increases yields and conversions of reactants. Metal molybdates have attracted interest because of their interesting structural, electronic, and catalytic properties.

A bimetallic ammonium nickel molybdate catalyst that was dispersed in supercritical methanol was investigated for the hydrodeoxygenation (HDO) of bio-oil by Yang T and co-workers [152]. In their study, the effect of both temperature and moisture in the HDO process were investigated. Their findings showed that increase in temperature led to high catalytic activity for HDO. The yield of hydrocarbons produced was the highest at the temperature of 370°C.

The alkali promoted α -NiMoO₄ and β -NiMoO₄ were synthesized and used by Martin-Aranda *et al.*[153] in the selective oxidation of butane. The main oxidation products were 1-butene, 2-butene, 1,3-butadiene, carbon monoxide and carbon dioxide. The results showed improvement in the total conversion of butane with an increase in temperature. As expected, the α -NiMoO₄ showed more

activity while β -NiMoO₄ showed more selectivity towards the formation of butenes. The addition of alkali promoters had a negative effect on the conversion of butane in both NiMoO₄ phases. However, the selectivity toward C₄ alkenes improved, with the addition of a more basic alkali resulting in an improvement of the yield.

Sorbitol was converted to hydrocarbons via the HDO process using NiMoO₄ and catalysts derived from NiMoO₄ by Qui et al.,[154]. They reported high yields of 87.5% alkanes with most products being cyclic alkanes. Their studies showed that the performance of Ni@MoO_x catalysts was due to synergistic effects between Ni⁰ and amorphous MoO_x species. They found out that the existence of Ni⁰ helped in the reduction of Mo⁶⁺ species which in turn improved the hydrogenation capacity of partially reduced MoO_x species. They also found Ni⁰ helped in stabilizing Mo⁵⁺ and Mo⁴⁺ that were found in the surface of the reduced Ni@MoO_x, which was essential for selective HDO.

Research has also shown that alloying of metals also improves the activities of catalyst. When comparing alloys of nickel molybdenum catalyst to its mono metallic counterparts, the alloys were found to be more active. The catalytic activity was found to decrease in this order, NiMo > Mo > Ni[134]. It is very important to understand the role of each metal in a mixed metal catalyst. Durr *et al.*[155], investigated the role of molybdenum in NiMoO₄·H₂O. It was concluded that during the reaction NiMoO₄·H₂O was transformed into γ -NiOOH which was the active catalyst for water oxidation. Molybdenum was found to play the role of morphology inducing agent, increasing the surface area of the active catalyst.

Nickel based catalysts are prominent in the conversion of FAMES to green diesel. Its abundance and cheaper price is making it more attractive. In this study the decarboxylation of methyl palmitate using binary Ni/Mo catalysts were investigated theoretically, and the results are discussed in Chapter 6. The reactive force field (ReaxFF) molecular dynamics will be used in this study. Results of the study yield more insight into the mechanisms of the reaction, which may be useful for further improvements in the design of the catalyst. Different catalyst planes and polymorphisms will be investigated. Computational techniques for the study will be described in CHAPTER 3.

CHAPTER 3

OVERVIEW OF COMPUTATIONAL METHODS

3.0 Molecular dynamics studies

Computer simulations can be used to study the structural, electronic, and dynamical properties of materials. Simulations can provide insight which can be applied to solving problems such as in the design of new catalysts and novel materials, understanding disease pathways, applications in drug design and development etc.[156]. Using computer simulations, the time required to develop new materials can be reduced as it helps narrow the selection of promising materials before laboratory trials that require expensive chemicals are conducted. Additionally, simulations act as a link between theory and experiment. The results from computer simulations are compared to experimental results to test the experimental theories and at the same time experiments that are difficult or impossible in laboratory settings can easily be performed. These experiments include working at very high temperatures, pressures and with hazardous materials. A simulation can also aid in predicting mechanisms of reactions as it can capture the position and movement of every atom at every point in time, which is impossible to do with any experimental techniques. Using computer simulation, the reaction conditions are carefully controlled, which can then be compared to simulations which were performed under different conditions. From this the effects of different conditions can be identified[157]. Computer simulations are thought of as a computational "microscope" that allows researchers to study the atomistic interactions that take place between different types of molecules [157].

Molecular dynamics simulation is a computer simulation technique used to study the movements of atoms and molecules which are interacting. Newton's second laws of motion is used to predict each atom's position as a function of time. The forces that are exerted on each atom by interacting atoms are repeatedly calculated and then using updated forces, the position and velocity of each atom are updated. The force, F_i acting on the atoms or molecules are derived from potential energy U (equation 3.1).

$$F_i = m_i \frac{\partial^2 r_i}{\partial t^2}, \quad 3.1$$

Where F is the force acting on particle i , m is mass and r_i is the position. The force is a negative derivates of potential energy (U) (equation 3.2).

$$F_i = -\frac{\partial U}{\partial r_i} \quad 3.2$$

The forces and positions are constantly calculated and updated in small time steps, and the system is then monitored some time to ensure that the temperature and pressure remain within the necessary levels. At regular intervals the coordinates are then written to an output file. The system's trajectory is defined as the coordinates as a function of time[157–160]. The system will typically achieve an equilibrium state after some initial changes. Averaging equilibrium trajectories can be used to extract the system's macroscopic characteristics from the output file.

3.1 Force field molecular dynamics

A force field (FF) is a set of energy functions and parameters that can be used to calculate the potential energy of a system of atoms or molecules, E_{sys} , as a function of molecular coordinates. These forces are derived from molecular mechanics force field which is then adapted to the findings of quantum mechanical computations and in some cases experimental results. There are three classes of force fields which include classical, polarizable and reactive force fields. In this study three types of force fields will be used, GROMOS and OPLS-AA force field which falls under classical force fields and ReaxFF which falls under reactive force fields. In molecular dynamics simulations, the potential energy is a sum of the non-bonded and bonded interactions according to equation 3.3. Figure 15 shows schematic representations of these interactions.

$$E_{sys} = E_{bonded} + E_{non-bonded} \quad 3.3$$

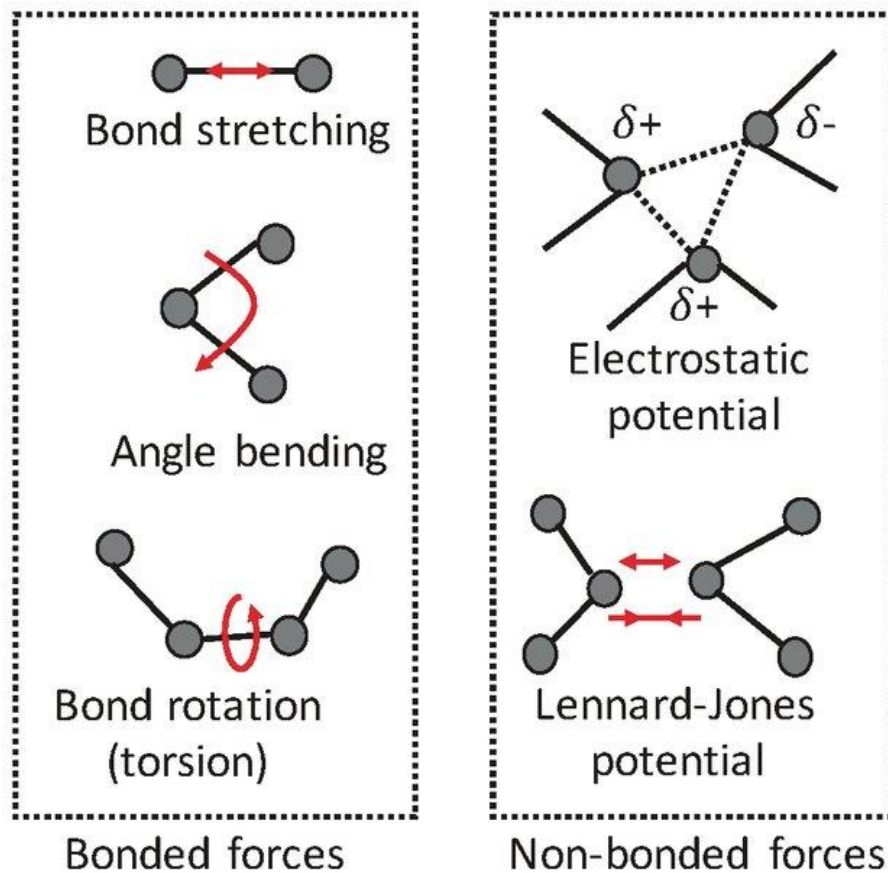


Figure 15: Schematic representations of forces contributing to the potential energy[161].

3.1.1 Bonded interactions

These are interactions between atoms in a molecule and are calculated using equation 3.4.

$$E_{bonded} = E_{stretch} + E_{angle} + E_{tors} + E_{improper} \quad 3.4$$

Where E_{bond} is used to describe bonding between two atoms, E_{angle} is used to describe three atom interactions and E_{tors} and $E_{improper}$ are four atom interactions. The contribution of each bonded interactions will be discussed in subsections 3.1.1.1 to 3.1.1.4.

3.1.1.1 Bonded interaction energy

The potential energy for bond stretching between two covalently bonded atoms is approximated by harmonic function. In here equilibrium bond length is given by l_o , bond length is l_i and k_i is the force constant (equation 3.5).

$$E_{stretch} = \sum_{stretch} \frac{k_i}{2} (l_i - l_o)^2 \quad 3.5$$

3.1.1.2 Bond angle potential

Harmonic potential is also used to describe the bond angle vibration between the angles ABC (equation 3.6). Here k_i is the force constant, ϕ_i is the actual angle, while ϕ_o is the equilibrium angle.

$$E_{angle} = \sum_{angle} \frac{k_i}{2} (\phi_i - \phi_o)^2 \quad 3.6$$

3.1.1.3 Torsions potential

The torsion potential energy is also known as dihedral angle potential is used to describe the change in potential energy arising from four sequentially bonded atoms. Torsional energy is periodic in the sense that it must return to its original value if rotated 360° . It is given by equation 3.7, where term n represents divisions of periodicity and ϕ is an angle and k_ϕ is a rotation barrier, is the torsion angles.

$$E_{tor} = \sum_{tor} k_\phi (1 + \cos n\omega) \quad 3.7$$

3.1.1.4 Improper dihedrals potential

Improper torsion dihedrals are potential energies for a group of four bonded atoms, with the central atom connected to the three surrounding atoms. The groups can be visualized as a pyramid, and the improper torsion potential is related to the distance between the central atom and the pyramid's base. This potential is mostly used to keep molecular structures flat and is intended to prevent aromatic rings from flipping to their mirror copies. The potential energy for improper dihedrals is calculated using equation 3.8. Where ϕ is a dihedral angle between the planes.

$$E_{improper} = \sum_{improper} k_\phi (\phi - \phi_o)^2 \quad 3.8$$

3.1.2 Non-bonded interactions

The non-bonded interactions are due to electrostatic interactions and van der Waals interactions. Coulomb equation is used to describe electrostatic interactions while van der Waals are calculated using the Lennard Jones potential. The total energy of non-bonded interactions in a system is calculated using equation (3.9).

$$E_{non-bond} = E_{vdw} + E_{cou} \quad 3.9$$

Where E_{vdw} is van der Waals and E_{Cou} is energy due to electrostatic interactions and these are dependent on the distance between pair of atoms.

3.1.2.1 Lennard Jones

Lennard Jones Potential or 6-12 interaction is used to calculate short-range potential energy that arises from non-bonding particles. These interactions are mainly due to the repulsive forces and attractive forces that result from induced dipoles. It is calculated using equation 3.10.

$$E_{vdw} = 4 \epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \quad 3.10$$

Where r_{ij} is the distance between interacting particles, ϵ is the depth of potential well while σ is the distance at which the potential energy is zero. According to the Lennard Jones model, the force between interacting atoms is dependent on the distance between the particles. If particles are very close to each other they will experience repulsive forces, if they are at moderate distance there is attraction between them because of the induced dipole moments while at infinite distances there do not interact with each other, and potential energy is zero. The repulsive terms are represented by r^{-12} while attractive represented by r^{-6} term is the equation.

3.1.2.2 Electrostatic interactions

Electrostatic interactions between two charged particles are calculated using equation (3.11)

$$E_{Coul} = \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad 3.11$$

Where ϵ_0 is the vacuum electric permittivity constant and q_i and q_j are the charges of particles i and j respectively, while r_{ij} is the separation distance between the charge centres. It arises because of differences in the electronegativity of the atoms. The electrostatic interactions converge slowly with distance making it computationally expensive to calculate. The algorithms

are often used to help expedite the calculations of electrostatic interactions. In this research, the Particle Mesh Ewald (PME) algorithm was used. PME decomposes coulomb potential into two parts, the fast decaying, and the slow decaying part. The fast-decaying part is short ranged and is computed in real space. The potential energy here is the sum of the contributions of all particles within the cut-off radius. The slow decaying part is long ranged and is computed in the Fourier space or reciprocal space. In the reciprocal spaces the long-range interactions converge faster. PME results in high accuracy in the calculations and faster computations of long-range interactions.

3.2 Gromos force field

Groningen Molecular simulations (Gromos) is a force field that was developed at the University of Groningen in the Physical Chemistry Department. The force field was developed to study biomolecular systems and has been able to describe both the physical and chemical properties since its inception[156,160,162,163]. It uses simple harmonic motion to describe the bending and stretching of bonds[164]. The initial versions of this force field, GROMOS96, was parameterised to reproduce experimental spectroscopic and crystallographic structural data[165]. Through years of successive parameterization, the new versions of GROMOS force field were made and were able to reproduce the physical and thermodynamical properties of materials with greater precision compared to the initial model of 1980 [163,165,166]. The GROMOS 45A4 version, was found to be better in retaining structure of molecules, while GROMOS 53A6 version showed improved agreement with experimental data but had flaws when protein simulations were performed as it exhibited structural flaws. These versions of GROMOS force field were also found to underestimate the free enthalpies of hydration for polar molecules [167]. The GROMOS 54A7 force field was created with the aim of having a force field that can be utilized for simulations of both proteins and membrane studies [168]. The GROMOS 54A7 force fields showed improvements in the stability of conformations and folding of proteins. Several researchers have used the GROMOS force field to study interactions of organic molecules and solvents. Tascini and coworkers used it to help understand the interactions between sebum oil and water[169]. They found that triglycerides molecules at the water interface adopted trident shape. This conformation directed the glycerol group toward the water phase while the hydrocarbon moiety was directed away from the water phase[169]. The Gromos FF was also used by Roccatano et al., to study the effect of co-solvent 2,2,2-trifluoroethanol (TFE) in the

stability of peptides[170]. Through their findings, they were able to show that TFE only interacted weakly with non-polar residues which in turn enhanced stability of peptides. Mukherji et al., used Gromos FF to study the conformational changes of polymers in different solution[171]. They were also able to monitor structural changes after addition of solvents. In the light of these findings, CHAPTER 4 of this thesis uses the GROMOS force field in order to show structural changes in triglycerides in the presence of solvents.

3.3 Optimized potentials for liquid simulations force field for all -atoms (OPLS-AA)

The OPLS-AA force field was developed by Jorgensen and coworkers [172]. Just like with GROMOS FF, bond stretching and angle bending energy are harmonic and can be calculated using equations (3.5 and 3.6). The Fourier series for dihedral angles is used to approximate torsional energy (equation 3.12)[172].

$$E_{(\phi)} = \frac{V_1}{2} [1 + \cos(\phi + f_1)] + \frac{V_2}{2} [1 - \cos(2\phi + f_2)] + \frac{V_3}{2} [1 + \cos(3\phi + f_3)] \quad 3.12$$

Where ϕ is the dihedral angle, V_1 , V_2 and V_3 are the coefficients in the Fourier series, and f_1 , f_2 , and f_3 are phase angles. Coulombic and Lennard-Jones interactions are used for non-bonded interactions (equation 3.13).

$$E_{ab(r_{ij})} = \left\{ \frac{q_i q_j e^2}{r_{ij}} + 4\epsilon_{ijj} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \right\} f_{ij} \quad 3.13$$

Where $E_{ab(r_{ij})}$ is the interaction energy between molecules a and b .

The OPLS-AA has been extensively used by researchers to investigate miscibility at atomistic level. The miscibility of polyoxymethylene dimethyl ethers and diesel blends were investigated by Mengwei et al., using OPLS force field. Through their study they were able to quantify mixing and de-mixing of the polymer and diesel blends. The electrostatic interactions were also found to play a major role in the mixing[173]. The structural and thermodynamic properties of triglycerides, their mixtures with water and interfaces with air were investigated by Ming and coworkers using OPLS-AA force field and coarse-Grained force field[174]. The results obtained were encouraging as they were able to reproduce experimental results. The force field has proven to be very efficient in reproducing structural and thermodynamical properties of organic mixtures. The OPLS-AA force field was therefore selected to study the thermodynamic

properties of ternary mixtures of triolein/methanol/cosolvent in CHAPTER 5 of this thesis [175–177].

3.4 Reactive force field (ReaxFF)

Quantum mechanical (QM) methods are the most efficient atomistic techniques for providing barriers and reaction energy for specific reactions. While QM-based methods can be used in dynamical simulations, these simulations are however limited to small systems and short time scales. This makes it difficult to use them to gain a detailed understanding of large systems such as mixed metal oxides, whose periodic surface cells could involve thousands of atoms[178–180]. Reactive force field (ReaxFF) was introduced by van Duin in 2001 to bridge a gap between QM calculations and Molecular Dynamics[181]. It is a bond order-based force field and uses parameters that are derived using few atoms using QM[179,182,183]. These QM derived parameters are then applied to a system with more than 100 atoms using ReaxFF making it to be computationally cheaper. ReaxFF can reproduce surfaces, structures, transition states and even energy barriers that were derived by QM calculations. Furthermore, it can find crucial configurations and high energy intermediates that other force fields cannot. Using ReaxFF, reaction conditions that are similar to experimental conditions can easily be modelled. These includes chemisorption, physisorption, rearrangements, high pressures, and high temperatures. In ReaxFF the bonded and non-bonded interactions are calculated separately and this enables it to be used in both covalent and ionic materials[178]. The guiding principles of ReaxFF includes:

- (1) The systems' energy and forces are a continuous function of bond distances, even during reactions.
- (2) Each element is defined by a single atom type, which allows the force field to be easily transferred to new systems while avoiding complicated atom type modifications during reactions. This is very important because during a reaction the atom character can change e.g., from sp³ to sp² to sp¹ and from electrophilic to nucleophilic.
- (3) There are no predetermined reactive sites and reaction pathways. This makes simulation using ReaxFF to be unbiased. The reactions can automatically handle changes in coordination that are associated with reactions, making it easy to uncover new reaction routes.

(4) The charge distribution on an atom is dependent on the environment it is in. This is because charge characteristics such as electronegativity, hardness, and shielding are tailored to recreate QM-derived charge distributions. The quantity of charge transfer is determined by the atoms' nature and the distances between them, and this allows atom charge distributions to fluctuate during reactions.

(5) All valence terms including bonds, angles, and torsions are bond order dependent. Bond orders are determined by distances between atoms, making it easier for the force field to identify and manage changes in atom connectivity during reactions.

(6) Non-bonding interactions including van der Waals and electrostatic interactions are included between every atom pair, independent of connectivity. The shielding term is then introduced to avoid excessive short-range attractions and repulsions.

Since being introduced in 2001, ReaxFF has developed rapidly, and the force field parameters have been developed to cover both catalysed and uncatalyzed organic systems[178]. The studied systems includes oxidative dehydrogenation of alkanes[179,182], pyrolysis of triglycerides[138,140,184,185], combustion[182,184,186] . Table 3. 1 shows some of the studies in which ReaxFF has been used.

Table 3. 1: Reaction and reaction conditions in which ReaxFF was used to study organic molecules.

Reaction	Time step	Simulation Time	Thermostat	Temperature	Reference
Oxidative dehydrogenation of methanol on V ₂ O ₅ slab	0.25ps	250ps	Berendsen	Dual Slab-650K System-2000K	[179]
Formation of acrolein from propene on BiMoO _x	0.25ps	125ps	Berendsen	Dual Slab-500K System-1500-2500K	[183]
Pyrolysis of methyl linoleate	0.1fs	1000ps	Nose-Hoover	2273.15	[184]

Reaction	Time step	Simulation Time	Thermostat	Temperature	Reference
Supercritical gasification of lignin	0.1fs	1ns	Berendsen	1000-5000K	[187]
Pyrolysis of tripalmitin	0.1fs	500ps	Nose-Hoover	1500K and 2000K	[136]
Pyrolysis of unsaturated triglyceride	0.1fs	500ps	Nose-Hoover	2000-2500K	[137]
Pyrolysis of oleic type triglyceride	0.1fs	100ps	Berendsen	300-2800K	[138]
Oxidation of Butane over a covered Cr ₂ O ₃ catalysts	0.1fs	150ps	Nose-Hoover	800-2000K	[188]

The system's total energy according to ReaxFF is the summation of several energy components as shown in equation 3.14.

$$E_{sys} = E_{bond} + E_{over} + E_{angle} + E_{tors} + E_{vdW} + E_{coul} + E_{under} + E_{specific} \quad 3.14$$

Where, E_{bond} is the energy involved in bond formation described as a function of interatomic distance. E_{tors} and E_{val} are energies associated with three-body valence angle strain and four-body torsional angle strain, respectively. E_{over} is an energy penalty that is used to prevent over coordination in atoms. This ensures that valence rules of atoms are followed and there is energy penalty that is introduced if an atom forms more than allowed bonds. The E_{under} is also a bond order parameter and is used for under coordinated atoms. E_{Coul} and E_{vdW} are non-bonding interactions that are due to electrostatic and dispersive contributions. They are calculated for all interactions between all atoms, without considering their bond-order and connectivity. $E_{specific}$ represents system-specific terms that are not normally included unless they are required to capture features related to the system of interest [178]. These include E_{lone} , due to lone-pairs, E_{Conj} due to conjugation, E_{HB} due to hydrogen bonding [178]. The detailed description of these

terms together with associated equations can be found elsewhere[179]. In this thesis the parameters that were developed by Vasenkov et al. [189] were used. The ReaxFF parameter sets were developed for the Mo/Ni/C/O/N/S/H system. They were used to study the atomistic details i.e., physical and chemical properties of complex fuel combustion.

3.5 Energy minimisation methods

Energy minimization is a crucial step in every molecular dynamic calculation. It involves finding a spatial arrangement of a group of atoms in which the net inter-atomic force on each atom is as close to zero as possible based on a computational model of chemical bonding. Using mathematical optimization algorithms, energy minimization starts with a non-equilibrium configuration and moves atoms to minimize net forces on them until they reach zero and the second derivatives become positive. (Equation 3.15).

$$\frac{\partial U}{\partial r} = 0 ; \frac{\partial^2 U}{\partial r^2} > 0 \quad 3.15$$

Where U is the potential energy and r is the coordinate of the system.

The most common methods used for geometry optimisation are derivative-based and use the gradient of the potential energy. The steepest descent [190] and conjugate gradient [191] methods are examples of first derivative methods.

3.6 Ensembles

Molecular Dynamics (MD) simulations are performed under different conditions known as ensembles. These ensembles provide a way to calculate the thermodynamic properties of the system. The choice of ensemble depends on the property one wants to estimate. There are several ensembles used in MD simulations, including isothermal-isobaric (NPT), canonical (NVT), and microcanonical (NVE) ensembles. These ensembles are briefly described in the following subsections.

3.6.1 Isothermal isobaric ensemble (NPT)

In isothermal isobaric ensemble, the number of particles (N), temperature (T) and pressure are maintained constant. It is used to simulate chemical reactions that are usually carried out under constant pressure experimentally. During NPT run, the volume of the system is constantly adjusted to maintain the set pressure. This is done by allowing the dimensions of the simulation

box to change. The temperature is regulated using a thermostat and the pressure is adjusted using a barostats.

3.6.2 Canonical or NVT ensemble

Canonical ensemble molecular dynamics simulations are conducted under a condition of constant number of particles (N), volume (V) and temperature. Here the energy and pressure of the system are allowed to fluctuate. The volume and temperature of system are allowed to remain constant using external thermostats.

3.6.3 Micro canonical ensemble (NVE)

This ensemble corresponds to an isolated system in which there is no exchange of heat or matter with the surrounding environment. Here the number of particles (N), volume (V) and the total energy (E) of the system are kept constant. The total energy is the summation of Kinetic energy and Potential energies which are allowed to fluctuate. The temperature and pressure of the system are allowed to fluctuate during the simulation run.

3.7 Thermostats

In molecular dynamics calculations the temperature of the system is calculated from the kinetic energy according to equation (3.16)

$$E_{kin} = \frac{3}{2}NK_B T \quad 3.16$$

Where E_{kin} is the average kinetic energy, N is the number of particles, K_B is the Boltzmann constant and T is the temperature. In MD simulations “thermostats” are used to ensure that the average temperature of the system remains constant. In this study the canonical (NVT) and isothermal isobaric ensembles are used for the calculations. These require the average temperature to be kept constant. The Nosé-Hoover and Berendsen thermostats were used to achieve constant average temperature.

3.7.1 Berendsen thermostat

Berendsen thermostat is used to maintain the average temperature of the system constant. This is accomplished by coupling the system temperature to an external heat bath with a constant temperature T_o . The velocity is adjusted at each step to ensure that the temperature changes proportionally with the difference in temperature.

$$\frac{\partial T(s)}{\partial t} = \frac{1}{\tau}(T_o - T(t)) \quad 3.17$$

Where τ is the coupling constant, which determines how the tight the water baths and system are coupled together. The velocities are scaled so that the change is proportional to the temperature difference between the system and the bath. The particle velocities are scaled by a scaling factor defined as

$$\lambda^2 = 1 + \frac{\delta t}{\tau} \left\{ \frac{T_o}{T(t-\frac{\delta t}{2})} - 1 \right\} \quad 3.18$$

Where $T\left(t - \frac{\delta t}{2}\right)$ is the leapfrog algorithm which is used for time integration.

3.7.2 Nosé-Hoover thermostat

Nosé-Hoover is another thermostat that is used to control the temperature of the system. To control the temperature of particles, a fictitious variable, ξ , is introduced. This variable acts as a thermal reservoir parameter that can either slow down or accelerate the particles until the desired temperature is achieved. By using ξ , the equation of motion can be expressed with the target temperature T_o and the instantaneous temperature T .

$$\frac{d\xi}{dt} = \frac{1}{Q} (T - T_o) \quad 3.19$$

Where Q is a parameter which is given by equation 3.20. τ is a time constant parameter.

$$Q = \frac{\tau_T^2 T_o}{4\pi^2} \quad 3.20$$

Following the modification of Newton's equation of motion, leapfrog integration must be modified as follows:

$$\xi\left(t + \frac{\Delta t}{2}\right) = \xi\left(t - \frac{\Delta t}{2}\right) + \frac{1}{Q} (T - T_o) \Delta t \quad 3.21$$

$$\xi(t) = \frac{1}{2} \left[v\left(t - \frac{\Delta t}{2}\right) + \xi\left(t + \frac{\Delta t}{2}\right) \right] \quad 3.22$$

$$v\left(t + \frac{\Delta t}{2}\right) = v\left(t - \frac{\Delta t}{2}\right) + \left[\frac{F_i}{m_i} - \xi \frac{r_i(t)}{dt} \right] \Delta t \quad 3.23$$

3.8 Barostats

Barostats are used to keep the pressure of the system constant. In molecular dynamics simulation, the pressure of the system is calculated using the equation 3.24.

$$P = \frac{Nk_B T}{V} + \frac{1}{3V} \langle \sum r_{ij} F_{ij} \rangle \quad 3.24$$

The equation consists of two components with the first component used to describe the pressure of an ideal gas with no interactions between the gas molecules. The second component is used to account for external forces that are acting on each gas molecule. There are several barostats that are used to keep the pressure constant, these include Berendsen[192], Nose-Hoover[193,194] , Andersen [195] and Parrinello-Rahman barostat[196]. Berendsen barostat has been found to improperly sample the system[192] while the Andersen barostat only allows isotropic deformations of the simulation box[195]. In this research the Parrinello-Rahman barostat, which is an extended version of the Andersen barostat, was used. The Parrinello-Rahman barostat allows both the size and shape of the simulation box to change.

3.9 Algorithms

3.9.1 Time integration

In MD simulation Newton equations of motion is solved for each atom. To solve it, it is important to know its position and its velocity at time (t). With this information, the position and velocity for next timestep ($t + \delta t$) can be approximated. When dealing with a system with a lot of interacting molecules finding solutions for each molecule and atoms is not feasible. To solve this, calculations are often divided into a series of very tiny time steps which are often 1 or 2 femtoseconds, ($10^{-15}s$) long. The forces and velocities are then computed for each timestep, and information generated is then used to compute new positions and velocities. The atoms are then moved to the new positions where set of forces and velocities are updated. This is done with the help of integrators. A good integrator must be reversible and energy conserving. The two commonly used integrators in MD simulations are Leapfrog and Velocity verlet integrator. In this thesis both were used.

Velocity verlet algorithm starts from the assumption that the acceleration does not change during a time step and uses Taylor expansions to estimate the next position and velocities according to equations (3.25 and 3.26)

$$\mathbf{r}(t + \delta t) = \mathbf{r}(t) + \delta t \mathbf{v}(t) + \frac{1}{2} \delta t^2 \mathbf{a}(t) + \frac{1}{6} \delta t^3 \mathbf{b}(t) + \frac{1}{24} \delta t^4 \mathbf{c}(t) + \dots \quad 3.25$$

$$\mathbf{v}(t + \delta t) = \mathbf{v}(t) + \delta t \mathbf{a}(t) + \frac{1}{2} \delta t^2 \mathbf{b}(t) + \frac{1}{6} \delta t^3 \mathbf{c}(t) + \dots \quad 3.26$$

$$\mathbf{a}(t + \delta t) = \mathbf{a}(t) + \delta t \mathbf{b}(t) + \frac{1}{2} \delta t^2 \mathbf{c}(t) + \dots \quad 3.27$$

Where $\mathbf{r}$ is the initial position, $\mathbf{v}$ is the velocity (first derivative), $\mathbf{a}$ is the acceleration (second derivative), $\mathbf{c}$ is the third derivative and so on. The initial positions, velocity and force at time t are then advanced to $t + \left(\frac{1}{2}\right) \delta t$ by integration.

$$v\left(t + \frac{1}{2} \delta t\right) = v(t) + \frac{1}{2} \delta t a(t) \quad 3.28$$

$$\text{where } a \text{ is calculated using: } a = \frac{f(t)}{m} \quad 3.29$$

The new positions are then given by equation (3.30)

$$r(t) = r(t) + \delta t v\left(t + \frac{1}{2} \delta t\right) \quad 3.30$$

From these the new forces are then calculated at the new times and updated.

$$f(t + \delta t) \leftarrow f(t) \quad 3.31$$

Using the new forces, the velocities for the new step can then be calculated from half velocities.

$$v(t + \delta t) = v\left(t + \frac{1}{2} \delta t\right) + \frac{1}{2} \delta t a(t + \delta t) \quad 3.32$$

The velocity verlet algorithm can be summarized in three steps being (a) The current position, velocity and forces of the system are used to obtain new position at the next time step, (b) after obtaining the coordinates of the new position then acceleration can then be derived from the new forces acting on atoms. The new acceleration is then used to calculate the velocity of the next position. The calculation of forces is the most expensive part of the simulation, and to minimise the cost, periodic boundary conditions (PBC), which restricts calculations to fewer atoms, is applied. This will be discussed in section 3.10. Selection of time step is also very important; small time-steps may give accurate results but are computationally more expensive while larger time steps though cheaper may not be accurate.

The Leap Frog algorithm is similar to velocity verlet algorithm with the difference being that velocities are not calculated at the same time as positions. Positions and velocities are updated at interleaved time points during leapfrog integration, staggered in such a way that they jump or “leapfrog” over each other.

3.9.2 Constraint algorithms

In MD calculation, constraint algorithms are used to constrain the bond length and angles. The equations of motion are modified with introduction of constraint forces acting in opposite directions along bonds. In this situation, the total energy of the simulated system is unaffected because the total work done by constraint forces is zero. Constrained simulation begins with an unconstrained phase, followed by modifications to satisfy constraints. There are several algorithms used to constrain bonds and angles and these include SHAKE, SETTLE and LINCS. In this thesis Linear Constraint solver (LINCS) was used to constrain bonds[197]. Compared to SHAKE it is time reversible, faster and has broader convergence conditions which decreases computation time.

3.10 Periodic boundary conditions

When carrying out a molecular dynamics' simulation, the particles that are being simulated on are put in a box or a unit cell. This unit cell is then surrounded by its replicated copies in all infinite directions forming a macro lattice (Figure 16). Under periodic boundary conditions (PBC) when a particle leaves the box on one side, the other will enter the box from the opposite side at the same velocity and this conserves the number of particles. PBC is applied to avoid problems with boundary effects caused by finite size.

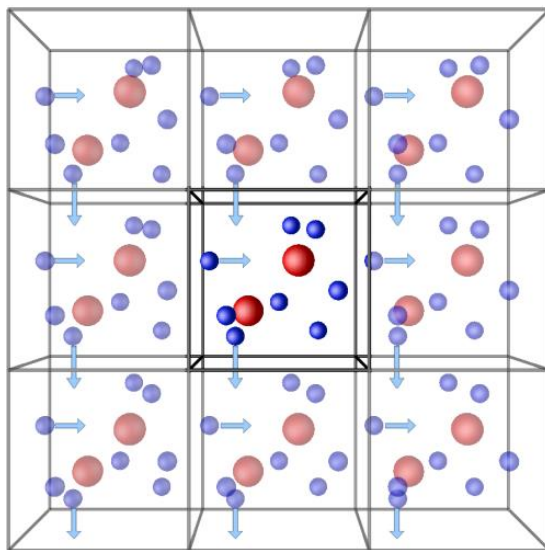


Figure 16 :Two-dimension periodic boundary box. The arrows show movement in and out of the box. Figure obtained from (<http://isaacs.sourceforge.net/phys/pbc.html>)[198]

The unit cell should be large enough that the molecule does not interact with its own image in the neighbouring box. A cut off radius is introduced when simulating the interactions between two particles to prevent molecules from interacting with their images. The cut off radius must not exceed half of the shortest vector of the box.

$$R_c = \frac{1}{2} (\|a\|, \|b\|, \|c\|) \quad 3.33$$

Where R_c is the cut-off radius a, b and c are the vectors of the unit cell.

The molecular dynamics simulations conducted in this thesis were carried out using three different software programs GROMACS[162,163], LAMMPS[199] and Amsterdam Modeling Suite (AMS) [200]. Chapters 4 and 5 utilized the GROMACS code, with the GROMOS force field applied in Chapter 4 and the OPLS-AA force field utilized in Chapter 5. Chapter 6 made use LAMMPS and AMS codes with the Reactive force field (ReaxFF).

CHAPTER 4

Molecular dynamic study of the interactions between Triglycerides and cosolvents binary mixtures

4.1 Introduction

Transesterification reaction has been found to be slow because of the poor miscibility of methanol with triglycerides[18,201]. This is due to the large differences in molar masses of the reactants and this causes a delay in reaction because of the resulting mass transfer limitation[202]. The poor miscibility is also due to the differences in the polarity of the main reactants, with oil being non-polar and methanol being polar. The successful collisions needed for the reaction to occur therefore do not happen frequently hence resulting slow reaction. To solve this predicament of a two-phase system that causes mass transfer lag, several solutions have been proposed, including agitation[53], high temperature reactions, use of longer chain alcohols[203], and use of co-solvents[43,53,59,77,80]. Agitation and high temperature reactions are energy-consuming processes which increase the cost of biodiesel production. Ethanol, being one carbon longer than methanol, has a higher solubility in triglycerides than methanol, whereas it is also safer and ‘greener’ as a solvent than methanol. However, the use of ethanol in transesterification is limited by the difficulty of separating the glycerol from the produced biodiesel in the presence of ethanol[204]. The use of a co-solvent is attractive because of the potential to recycle the solvent, which can lower the cost of production[15].

The presence of co-solvent has been found to reduce the mass transfer constraints encountered in the transesterification reaction. The addition of a cosolvent creates a single-phase system which aids in the dissolution of methanol in triglyceride. This not only speeds up the reaction, but also reduces energy consumption because stirring is not required, and it is even possible to perform the reaction at room temperature. Sawangkeaw *et al.*[75] studied the effect of using hexane and

tetrahydrofuran (THF) as co-solvents for the transesterification of vegetable oil, which they found to reduce the viscosity of the palm kernel oil, hence increasing the rate of transesterification. However, the reaction was conducted under supercritical conditions, which is a costly process on an industrial scale. Boocook *et al.*[15,97] used several ethers as co-solvents including dioxane, THF and diethyl ether (DEE), in the transesterification of different triglycerides. The solvents were selected depending on how close their boiling points were to the boiling point of methanol, which would make it easier to recover both co-solvents and excess methanol as they can be co-distilled and recycled. They were able to carry out the reaction at ambient temperatures without any mechanical stirring and they found that separation of glycerol was also four times faster in the presence of co-solvent and that, compared to other ethers, THF was the best co-solvent. These findings were also confirmed by Encicar *et al.*[53], who used several co-solvents, including DEE, THF and acetone, in the transesterification of rapeseed oil. They were also able to achieve high biodiesel yield in short reaction times, even at room temperature, where they found DEE and THF to be the most effective co-solvents, and DEE was easier to recover than THF.

Although THF, DEE and dioxane have been widely used as co-solvents for transesterification, they have the disadvantage of easily undergoing autoxidation to peroxide and they are soluble in water which makes their recovery difficult. These properties cause a serious safety concern regarding their use as solvents, as over time they tend to form explosive organic peroxides. For this reason, small quantities of peroxide inhibitors are often introduced in ethers to slow down their formation[78,103,104]. Cyclopentyl methyl ether (CPME) has proven to be useful as a green solvent, as it is stable and, unlike other ethers, does not form peroxides. Additionally, it has low solubility in water, low toxicity and it is stable under both acidic and basic conditions. It has been used in direct acid-catalysed transesterification of microalgae as a co-solvent and in purifying the produced biodiesel[106]. The effects of CPME in the rate of the reaction and product recovery were not reported. Even though CPME has a higher boiling point (106°C) than methanol (65°C), it is non-polar and can easily penetrate lipid material and completely dissolve it[35], which makes it a good co-solvent for triglycerides. Gamma valero lactone (GVL) is another green solvent with properties that make it a good co-solvent for biodiesel production. GVL has a boiling point of 205°C which is higher than that of methanol[205]. It also does not

form peroxides, which makes it safer for storage and transportation. GVL can be prepared from waste paper and has been used as an illuminating oil and lighter fluid [206], where it was found to burn cleanly with low emissions of volatile organic compounds (VOC). GVL is also a non-polar solvent which is able to dissolve lipids[207]. Its potential as a blending solvent for biodiesel and petroleum diesel was investigated by Bereczky et al., who found that the presence of GVL reduced the emissions of volatile organic compounds, without affecting engine performance[208,209]. GVL has the potential to be used as co-solvent, where it has another advantage over other solvents, as it is not necessary to remove GVL at the end of the process, because it is itself a fuel already.

Although there are many experimental studies on the use of co-solvents in the transesterification reaction[57,76,106], the theoretical investigations on the subject are still lacking, despite the importance of understanding the role of co-solvents in transesterification, which itself is a complicated reversible reaction. There have been no investigations on the molecular level interactions between co-solvent and triglycerides. Such investigation is important as it helps in narrowing the selection process of solvents that can be used in improving the miscibility of methanol in triglycerides. Molecular dynamics (MD) is a powerful tool that is used to characterize the structural and mechanical properties of systems to gain in-depth understanding of processes at the atomistic or molecular level. Such direct insight is not always easily obtainable from physical experiments[169,210,211].

This chapter describes a systematic molecular dynamics study of the physical and structural properties of binary mixtures of triglyceride, triolein, with several co-solvents and methanol. Triolein is the main constituent of olive oil. It is obtained from a condensation reaction between glycerol and oleic acid[212–214]. The transesterification of triolein in methanol results in the formation of methyl oleate, which is the second-most often occurring fatty acid methyl ester (FAMES) from plant produced biodiesel[215]. The intermolecular interactions between the triolein and the solvents can be affected by the polar group, the saturated and unsaturated sites[212]. It is interesting to find out how each part of the triglyceride molecule interacts with different co-solvent molecules. Co-solvents act by interacting with both the polar methanol and the non-polar part of triglycerides. Since triolein is largely non-polar due to its aliphatic chains, interaction of the methanol or co-solvent with the aliphatic side chains is essential for the formation of a one-phase triolein/methanol/co-solvent system. The aliphatic part of any co-

solvent is therefore critical for this interaction. This analysis provides information on the role of co-solvent interactions and their relationship to the overall solvation, which provides the basis for the development of a more cost-effective route for the production of biodiesel and give guidance on the properties that make a good co-solvent for transesterification.

4.2 Computational methods

Using molecular dynamics simulations, the interaction between triglycerides and certain co-solvents was investigated. Six binary mixtures of triolein and solvent used in this study were triolein/GVL, triolein/CPME, triolein/hexane, triolein/THF, triolein/1,4-dioxane, and triolein/diethyl ether. Figure 17 shows the structures of all the cosolvent molecules and triolein used. The GROMOS54a7 force field was used to describe all interactions between the molecules[216,217]. The force field parameters, including charges, were obtained through the Automated Topology Builder and Repository (ATB) engine[218]. The GROMACS software was used for constructing initial configurations, molecular dynamics simulations, and some of the analysis [156,162,163].

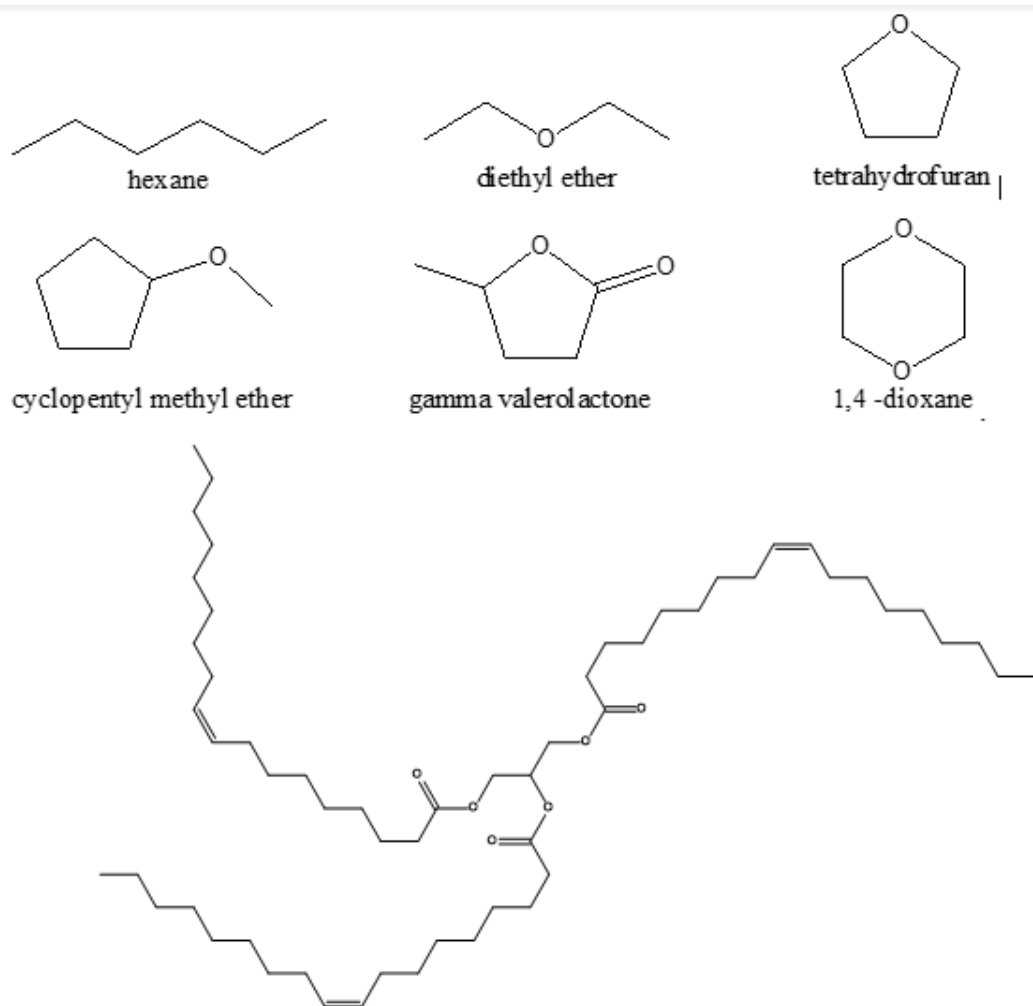


Figure 17: The structures of co-solvents and triolein used in this study.

4.2.1 Preparation of initial configurations

The first step in any MD simulation is the preparations of initial configurations. This was done by inserting 300 DFT optimized molecules of triolein molecules into a cube with dimensions of approximately 8 nm using GROMACS “insert” utility. The triolein molecules were then energy minimized to reduce the potential energy of the system. The steepest descent algorithm was used with energy convergence of $100\text{kJmol}^{-1}\text{nm}^{-1}$. The energy step size was set at 0.01nm while maximum minimization steps allowed were 50000. Verlet cut-off scheme was used for short-range van der Waals and electrostatic interactions with a cut-off of 1.2 nm. The long-range interactions were treated with Particle Mesh Ewald (PME) and cubic periodic boundaries were

applied. Figure 18 shows a typical plot of the change in potential energy during the energy minimization stages, which starts with a rapid decrease until it reaches a constant minimum.

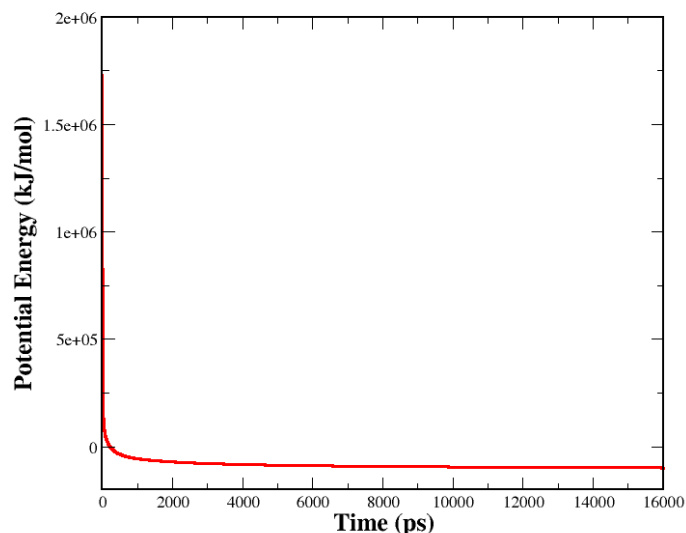


Figure 18: Potential energy of the system as function of time for steepest descent energy minimization stage, for a system consisting of 300 molecules of triolein and 3600 molecules of diethyl ether.

The energy minimization was followed by a short isothermal isochoric dynamics (NVT) simulation to relax the system to 298.15 K. The Leapfrog integrator was used to solve the equation of motion, with a time step of 1fs and simulation time of 100ps. Short-range and long-range interactions were treated the way they were under energy minimization. The system's temperature was kept at 298.15K using a Berendsen thermostat with a coupling constant of 0.1ps. The velocities were selected using Maxwell-Boltzman distribution from the set temperature. The Periodic Boundary Conditions were applied to the system in xyz directions.

The production runs were conducted under NPT ensemble starting from the NVT final configuration. For this part of the calculations, the leapfrog integrator was adopted, and the production runs were 100ns long. Key physical properties such as density and volumes were monitored during the simulations using the GROMACS utility “energy” to determine if the

system was well equilibrated (Figure 19). Simulations were done using a time step of 1fs. The system was run under constant pressure (1 bar) with Parinello-Rahman barostat. Pressure coupling was applied isotropically (which allows the box to change dimensions in xyz directions) and semi-isotropically (which only allowed the change in x and y directions) depending on the experiment. The compressibility was set at $4.5 \times 10^{-5} \text{bar}^{-1}$ and bonds were constrained using LINCS algorithm. Treatment of short-range and long-range interactions was the same as in earlier sections. After equilibration, the density of triolein at 298.15 K was found to be 911 Kg/m^3 which is comparable to the experimental value in the literature of 907 Kg/m^3 [80] (see Figure 20).

The equilibrated system was then elongated in the z axis, keeping the triolein molecules at the centre of the box. 3600 co-solvent molecules were then added to the empty space within the extended box, i.e., 1800 molecules to each side of the triolein, as shown in Figure 21. This was done to keep the ratio of oil to cosolvent to 1:12 which is commonly used experimentally[27,219]. Figure 21 shows the initial configuration visualized using VMD software[220].

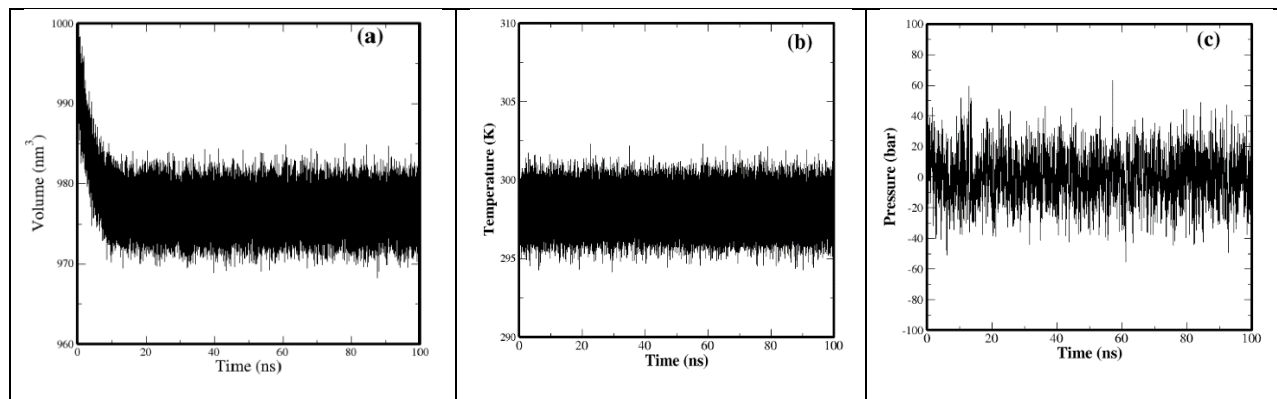


Figure 19: The change in volume (a), temperature (b) and pressure as a function of simulation time obtained during the NPT equilibration and production stage.

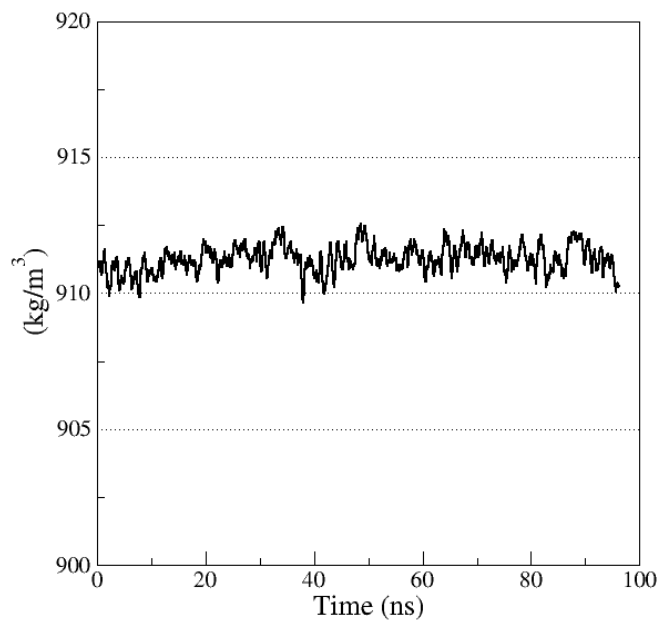


Figure 20: The change in density of triolein.

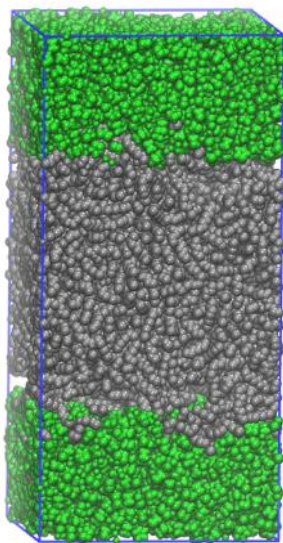


Figure 21: Initial configuration of system generated using gmx insert utility. Key: Grey represents triolein molecules and Green is diethyl ether molecules

Unless otherwise specified, the first 10ns of the trajectory were excluded from analysis, as it was considered part of the equilibration phase. Images of the systems were visualized with the VMD

program [220] and analysis of the trajectories was achieved using TRAVIS software [221,222] and GROMACS[156,163].

4.3 Results and discussion

4.3.1 Change in partial densities

Simulated mixing was analyzed by calculating the partial densities of the components across the z-direction of the simulation box using the GROMACS “gmx energy” utility and equation 4.1.

$$\rho_i = \frac{m_i N_i}{V} \quad 4.1$$

Where ρ_i is the partial density of the component i , m_i is the mass of a single molecule of i and N_i is the number of molecules of i and V is the total volume of the system. Figure 22 shows the change in partial densities of triolein (solid lines) and diethyl ether (dotted line) as the simulation progresses. From this figure we can see that as the simulation progresses co-solvent molecules move towards the centre of the box and exchange with the centrally located triolein molecules and vice versa, causing the partial densities to change. This continues until there is no change in the partial density as seen in the averaged 90-100 ns partial density. Snapshots of the simulation box corresponding to different simulation times are shown in Figure 23, from which the change in the molecule arrangement is clear. Presented in Figure 24 is the change in partial density for all binary mixtures studied. Here the focus was only in the first 10ns and last 10ns of the simulation. Plotted in dotted lines is the average partial density for first 10 ns of the simulation, while solid lines are partial densities in the last 10 ns. Within the first 10 ns, most of the system is still biphasic as the three regions along the z direction are still clearly noted. The density at the centre of the simulation box is approximately 911Kg/m³ which is similar to the reported literature experimental value for triolein of 907Kg/m³ [80,223], suggesting that the region still consists of triolein only. As the system propagates further, co-solvent molecules move towards the centre of the box and exchange with the centrally located triolein molecules and vice versa, causing the partial densities to change. For the solvents that are fully miscible with triolein, the partial densities graphs finally flatten out in the last 10ns. This behaviour was observed for CPME, hexane, diethyl ether and THF. For GVL and dioxane the graphs do not level off, showing that these two solvents are not miscible with triolein or that mixing is slower, Figure 24(c & f).

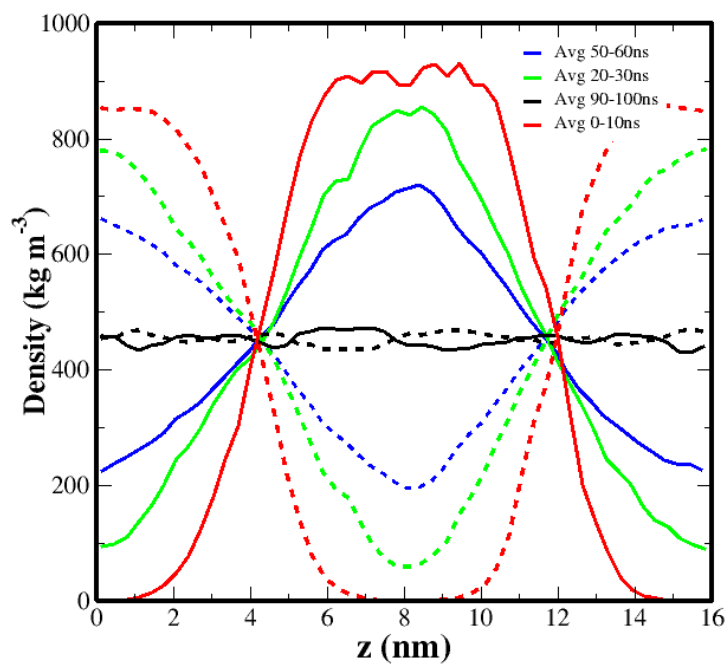


Figure 22: The change in the partial density as the simulation progresses. Plotted in dotted lines is co-solvent (Diethyl ether) and in solid line is triolein.

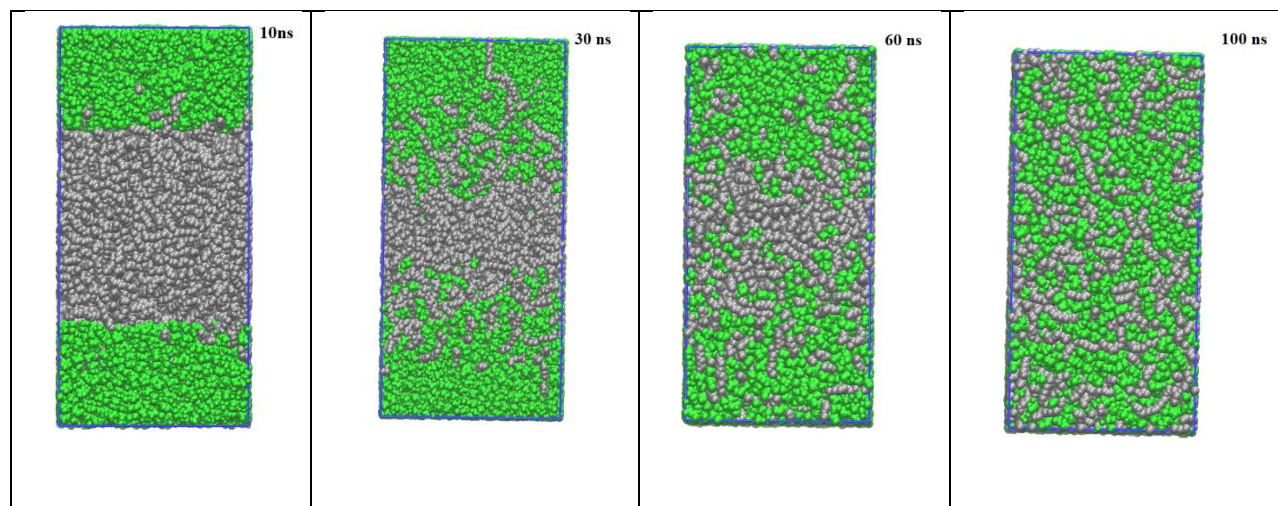


Figure 23: Snapshots of the systems captured at various simulation times to show the movement of molecules. Grey is triolein and green is solvent (DEE).

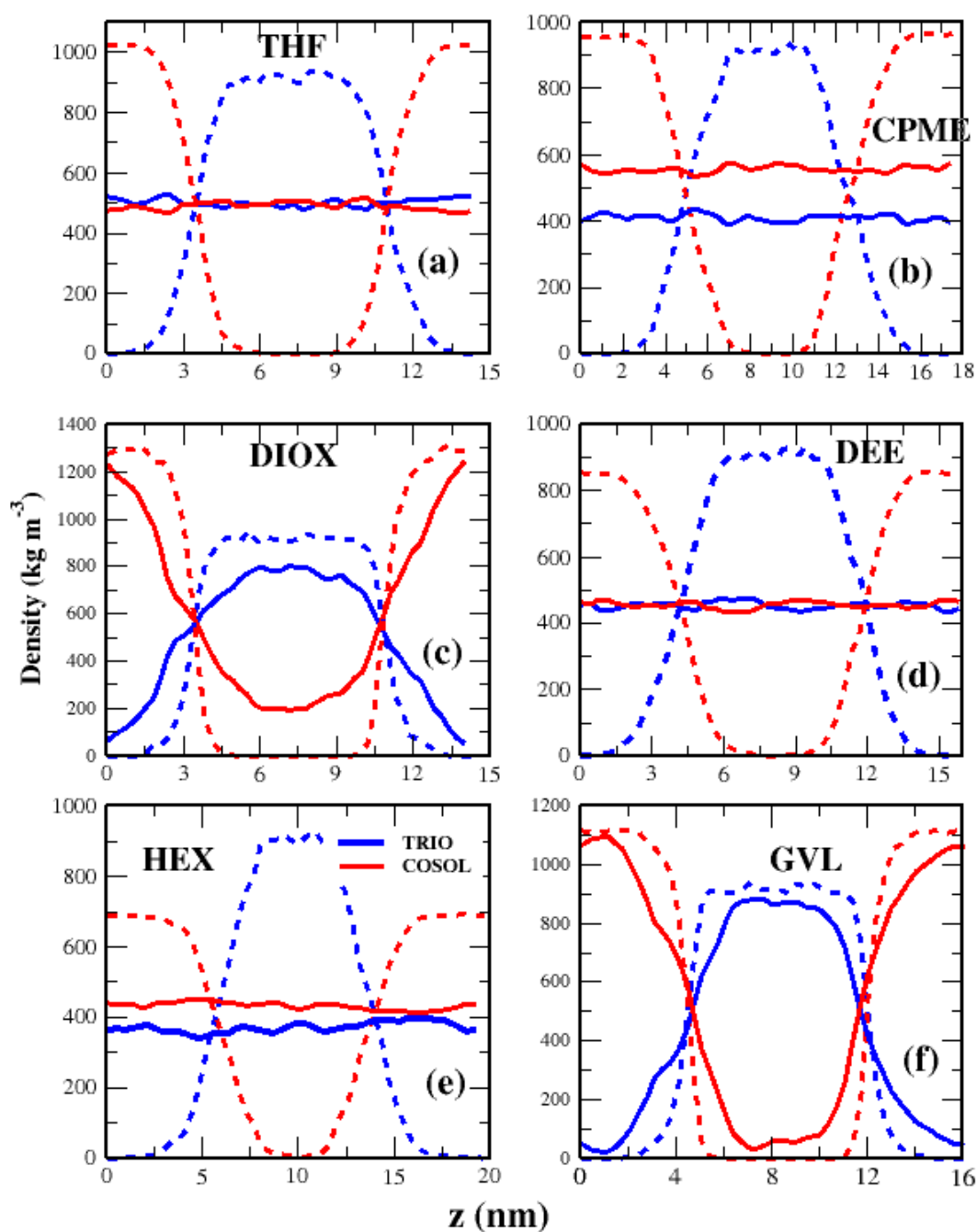


Figure 24: Change in partial density of Triolein and co-solvents. The first 10 ns are shown by broken lines while the last 10 ns is solid line. (a) THF, (b) CPME, (c) Dioxane, (d) DEE, (e) Hexane and (f) GVL.

Triolein/GVL and triolein/dioxane simulations were repeated at 333.15 K which is the temperature most commonly used in transesterification reactions [19,31]. The partial densities obtained are shown in (Figure 25(a and b)). For triolein/dioxane system partial densities in the last 10ns flattened out especially in the centre of the box which originally had only triolein (Figure 25(a)). For the triolein/GVL mixture (Figure 25(b)), significant changes in partial densities were observed, indicating better mixing of triolein, and GVL molecules. However, the graphs did not level off, showing that its mixing is still slow even at 333.15K.

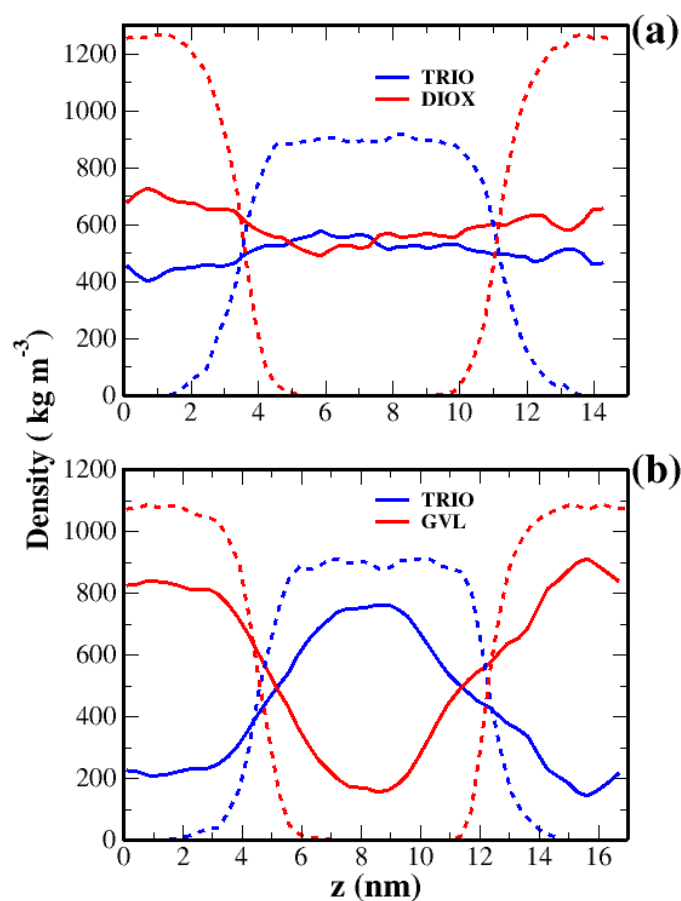


Figure 25: Partial Density of (a) triolein/dioxane and (b) triolein/ GVL mixtures at 333.15K.

4.3.2 Solvent distribution around triolein molecule

Densities of co-solvent molecules around different regions of triolein relative to the bulk densities were calculated using TRAVIS[221]. Three regions were selected as shown in Figure 26. The geometrical regions are defined as cylinders with a 0.600 nm radius. The three regions

are defined as the region bounded by the atoms C1-C5 (polar part of triolein where carbonyl oxygen and ester oxygen are located), C6-C15 (region including the C-C double bond) and C13-C19 (entirely saturated part of the hydrocarbon chain). The relative densities reported here are for the entire 100 ns simulation and running averages are reported. The relative densities are shown in Figure 27. Apart from dioxane and GVL all the graphs are characterised by three regions: first an initial rapid increase in the relative densities, followed by slowing down, and finally a flat region which represents complete mixing of the co-solvent and the triolein. The equilibration time is approximately 20 ns for DEE, THF and hexane and 30 ns for CPME. GVL and dioxane do not reach equilibrium, as shown in Figure 27 (e-f), in agreement with the results obtained from the partial densities which show that they do not mix with triolein.

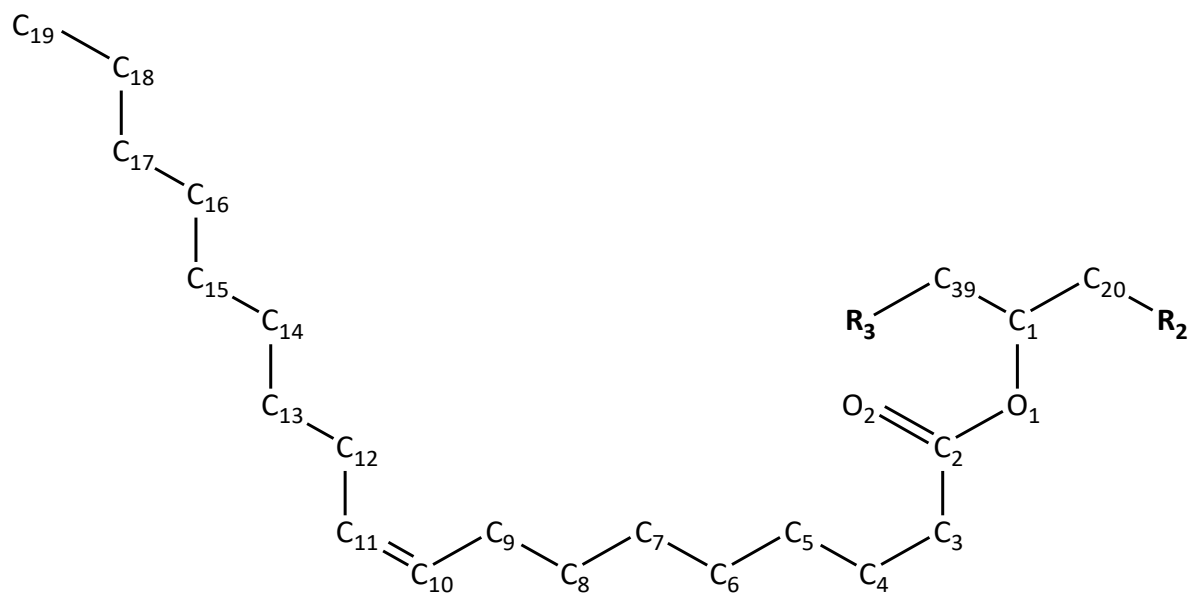


Figure 26: The numbering scheme for triolein R_1 chain as used in text. R_1 chain starts at O_1 and ends at C_{19} . $R_1 = R_2 = R_3$

Hexane, which is the only alkane used in this study, has been used before as co-solvent in biodiesel production[75]. As expected, it has higher affinity to the saturated hydrocarbon region, C13-C19 (the local density is approximately equal to bulk density) than to the other two regions (local density is lower than the bulk density in those regions). The flexibility and shape of the hexane molecules also makes it easier to pack side by side around the triolein chain which leads

to a higher density. The van der Waals forces between hexane and the C13-C19 region are stronger, which results in strong attraction.

In THF/triolein mixtures (Figure 27(a)), the local density of THF around the regions C1-C5 and C13-C19 are slightly higher than the bulk density after 20 ns of simulation time, showing that these regions have a high affinity for THF molecules[224]. THF is an aprotic solvent with a dielectric constant of 7.6[225]. It is a slightly polar solvent that can dissolve a wide range of non-polar and polar compounds. As such, it has an affinity to both polar and non-polar regions of triolein. The attraction in region C6-C15 is slightly weaker, which is attributed to steric hindrance from double bonds, which makes packing of THF molecules difficult.

Figure 27(b) shows the local densities of CPME around specified triolein regions. The levelling of the plots takes a bit longer in CPME than THF, showing that it mixes more slowly. The relative densities around C1-C5 and C13-C19 are also higher than at the C6-C15 region [224]. CPME is also a non-polar solvent [78] which explains its high affinity to the C13-C19 region. CPME has a methyl group which might be responsible for slower mixing than seen with THF. Diethyl ether displays similar behaviour to THF and CPME, see Figure 27(d). The DEE molecule is straight, like hexane, which results in compact packing and a preference for the C13-C19 region.

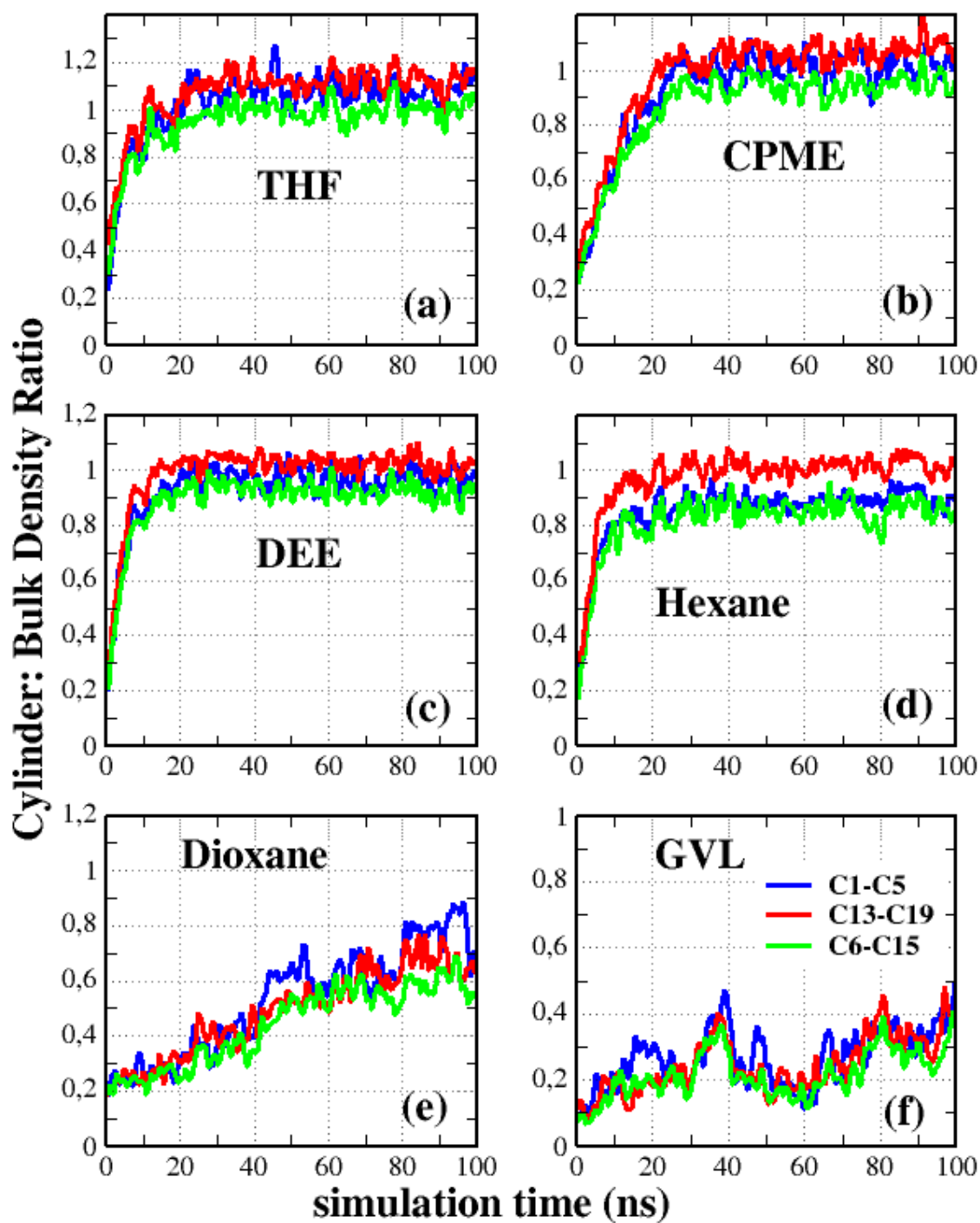


Figure 27: Density ratio of co-solvents near different triolein regions and in bulk solution. (a) THF, (b) CPME, (c) DEE, (d) Hexane, (e) Dioxane (f) and GVL and (see Figure 26 for definition of the triolein regions).

In GVL/triolein, and dioxane/triolein mixtures (Figure 27(e-f)), the local densities around all the triolein regions are much lower than 1, showing that the triolein/triolein and solvent/solvent interactions are favored compared to triolein/solvent interactions. It should be noted that in the case of dioxane, the density was still rising even after 100 ns, suggesting that it might mix with triolein after longer simulation times or at higher temperatures.

The results of calculations of relative densities at 333.15K are presented in (Figure 28) for binary mixtures of triolein/dioxane and triolein/GVL. From these, it can be noted that the three distinct regions, (rapid initial increase, slowing down and final constant density ratios) that were observed at 298.15K in CPME, THF, DEE and hexane are not clearly defined/visible in Figure 28(a). There is rapid increase in the density ratio that only appears to be slowing down at around 60 ns. We can therefore conclude that the dioxane still mixes more slowly than THF, hexane, CPME and DEE as it does not reach equilibration before 80 ns even at a higher temperature. This might be largely due to it being a denser liquid, in fact its density is higher than that of triolein[107,226]. Dioxane shows affinity for the polar (C1-C5) and aliphatic (C13-C19) regions in triolein, made possible by the ability of dioxane to exist in combination of chair and boat conformations. The chair conformation is non-polar, whereas the boat is polar[107]. The triolein/GVL local density is still much lower than the bulk density even at 333.15K. The higher temperature only improves the attraction between triolein and GVL slightly. The relative densities are still lower than 0.6 at 333.15K which shows that GVL self-interactions are stronger than GVL/triolein interactions[227].

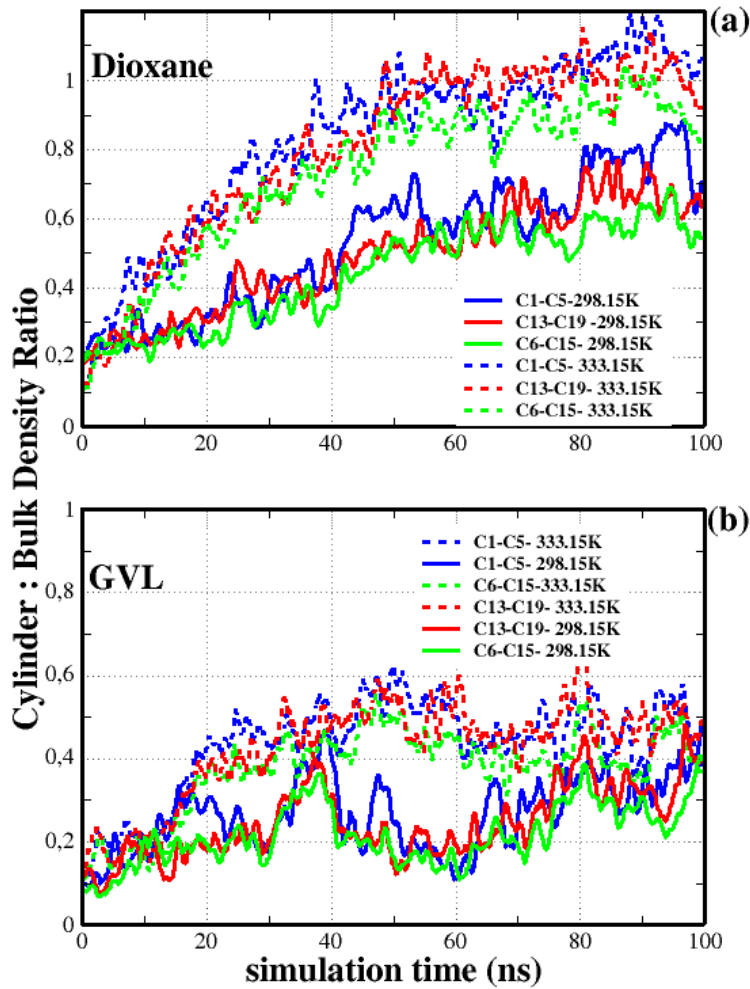


Figure 28: Density ratio of co-solvents near different triolein regions and in bulk solution. triolein/dioxane (a), triolein/ GVL and triolein/Dioxane binary mixtures. Plotted in solid lines is the density ratios at 298.15K and dotted lines is at 333.15K.

4.3.3 Radial distribution functions

Radial distribution functions (RDF) are used to measure the probability of finding an observed particle at a certain distance from the reference molecule. An RDF value greater than 1 shows that the probability of finding a particle at that radius from the reference point is greater than the uniform probability [222]. It is calculated using equation 4.2.

$$g(r) = \frac{\text{Pr}(r)}{4\pi r^2 \rho_o} \quad 4.2$$

Where Pr is the probability density of finding a particle at any point with the distance r from the reference particle and ρ_o is the mean number density. RDFs of the center of mass (COM) of the solvent molecules from the triolein carbon atoms C1 (C1-COM) and C11 (C11-COM) were calculated and are presented in Figure 29(a & b). The distribution functions display typical behavior for liquids, which show progressively weaker order at longer distances. The strongest peak is centered at 5-6 Å and a second one at around 9 Å, followed by a smooth, broad peak at a longer distance of around 14 Å. These three peaks are present in all triolein/co-solvent mixtures and are similar to those observed by Tascini et al. [169] when studying the interaction of tri-cis-6-hexadecenoin with water. The first peak for THF is very sharp and appears at 5 Å, showing a strong interaction between THF and triolein. The CPME peak appears broader and slightly shifted to longer distances compared to THF. Peaks appearing at longer distances include those for GVL, hexane and diethyl ether. The peak for GVL has the lowest intensity, showing that there is weaker order in the arrangement of GVL molecules around the C1 of triolein. There is also a small shoulder on the left of the main C1-COM RDF, indicating a weak interaction between the polar region of triolein with the acidic hydrogen of GVL. The calculated radial distribution functions for the interaction of the non-polar part of triolein with co-solvents, C11-COM (co-solvents) are presented in Figure 29(b) and Figure 30. The three peaks that were observed in the C1-COM are still present, but the positions of these RDF peak maxima and minima are slightly different. The intensities of the C11-COM peaks are weaker in GVL, THF and dioxane compared to C1-COM, but for hexane and DEE, the C11-COM peaks have higher intensity. This is understandable given that the shape of the latter two molecules can easily be arranged in an orderly manner around the hydrocarbon chains. For CPME there were only minor differences in C1-COM and C11-COM. It has been observed that for GVL (Figure 30(f)), which does not mix with triolein, the peak maxima of both C1-COM and C11-COM are below 1. On the other hand, for mixtures that do mix, the peak maxima are above 1. The intensity of the peaks of both C1-COM and C11-COM in dioxane and GVL mixtures increased with an increase in temperature from 298.15 K to 333.15 K. However, the shapes and RDF peak maxima remained unchanged, indicating that the coordination shells of triolein and these solvents are unaffected by temperature changes. Only the probability of the interactions changes, as demonstrated by the increase in peak height showing higher correlations (Figure 31). Even though the $g(r)$ for C1-

COM and C11-COM increased with temperature for both systems, it was still lower than 1 (asymptotic value) for triolein/GVL, showing that the system is not fully mixed.

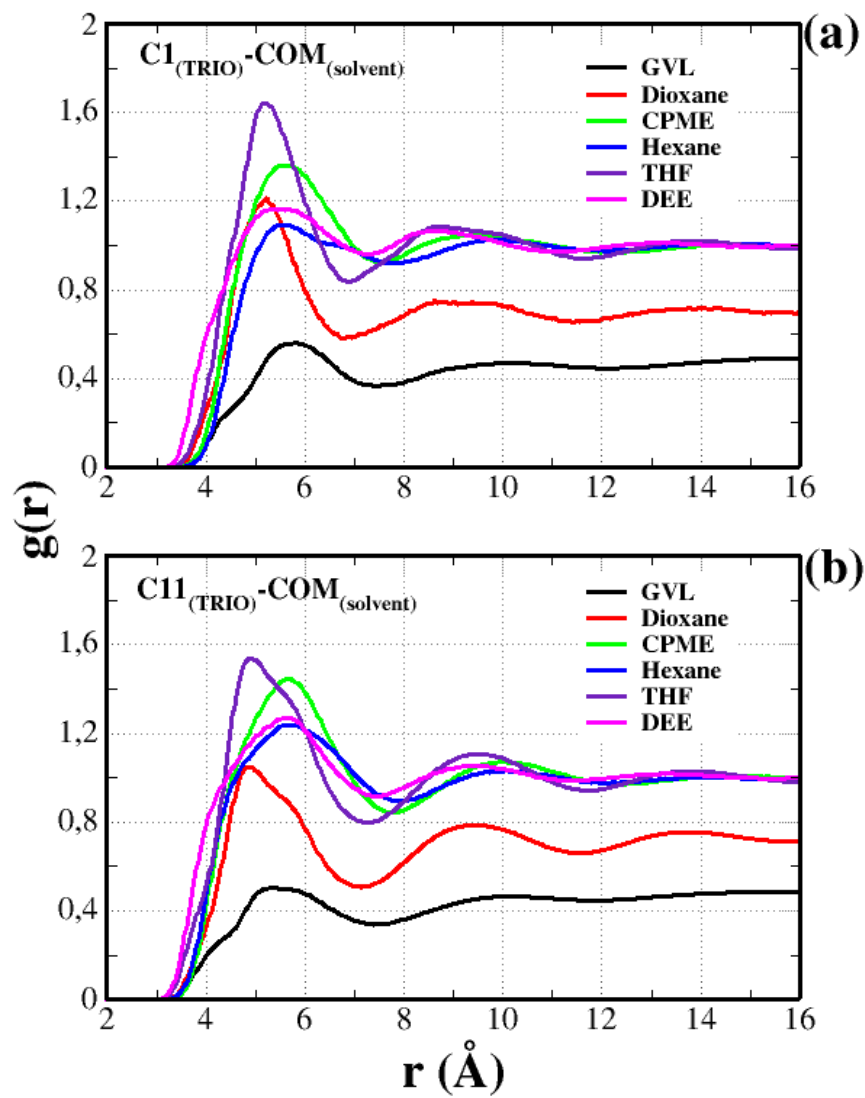


Figure 29: Radial distribution function (RDF) (a) C1-triolein and centre of mass of co-solvents and (b) C11-triolein and centre of mass of co-solvents.

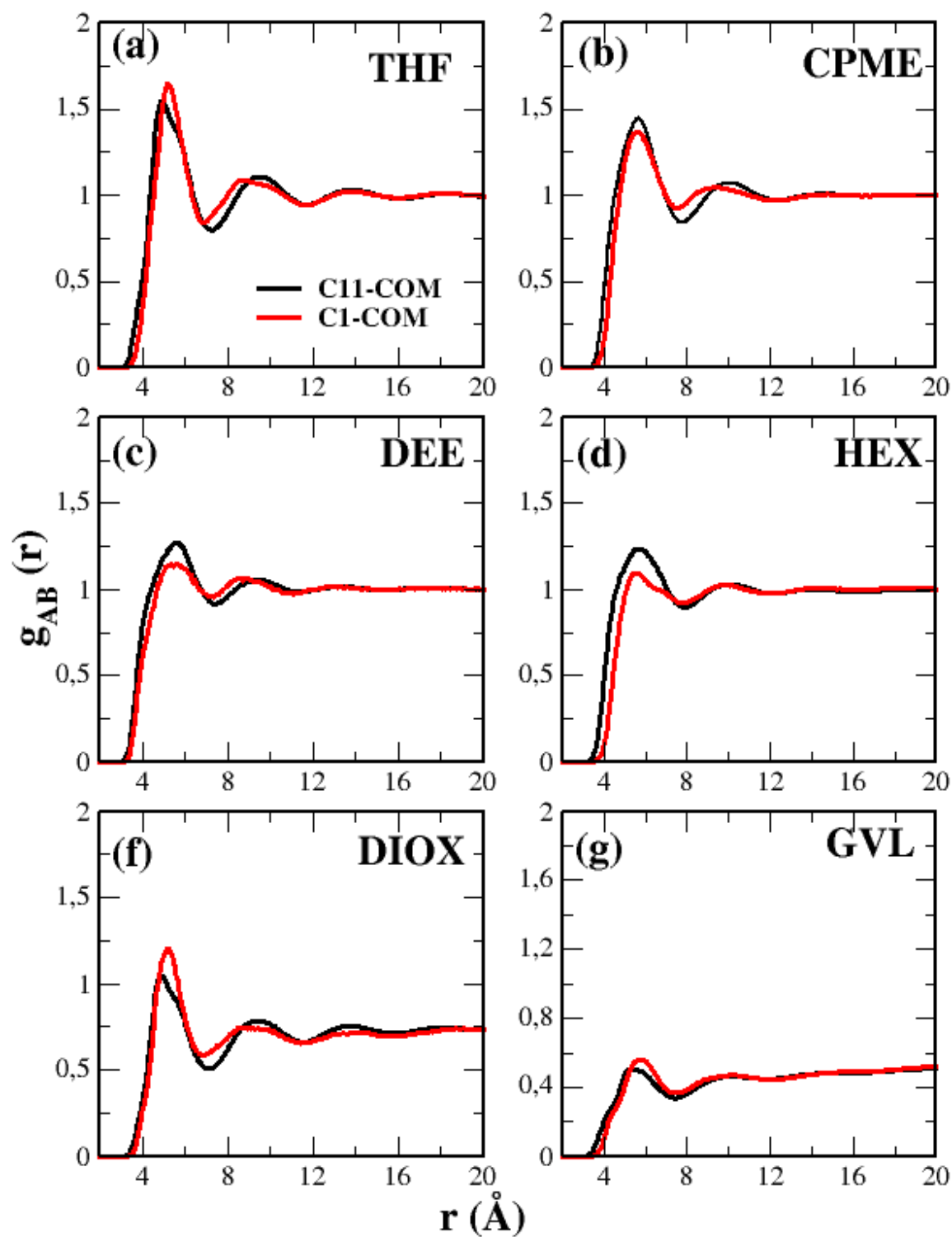


Figure 30: C1-COM and C11-COM radial distributions functions. (a) THF, (b) CPME, (c) DEE, (d) Hexane, (e) Dioxane and (f) GVL. (See Figure 27 for atom numbering)

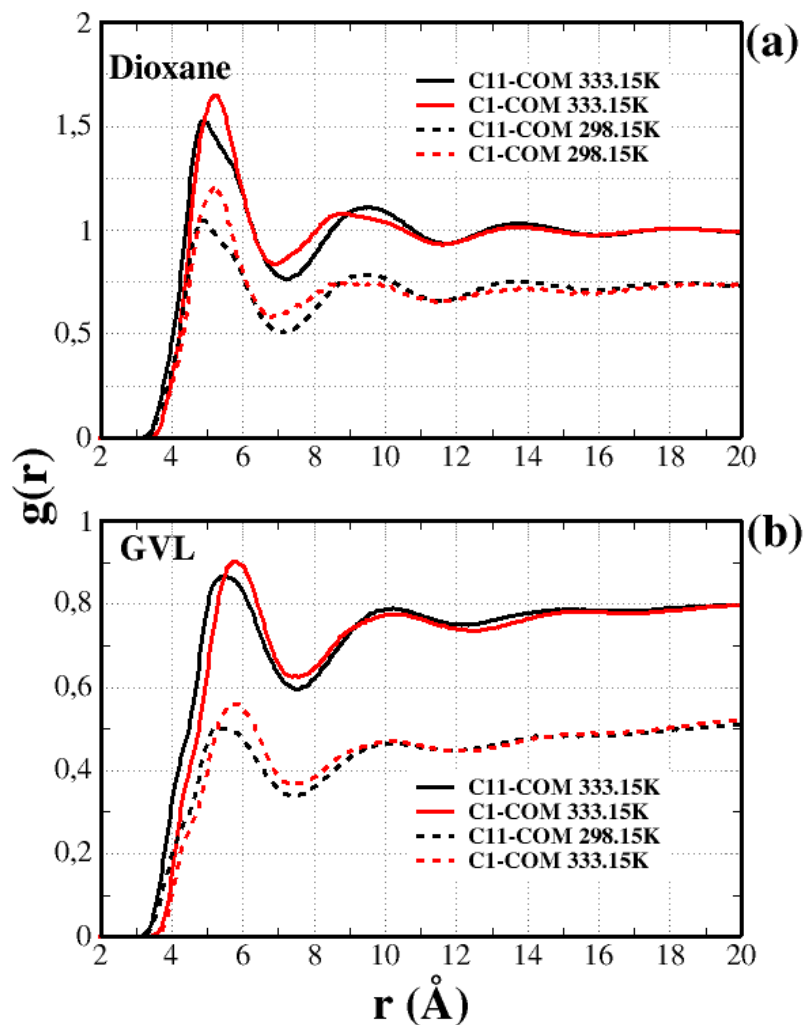


Figure 31: Radial Distribution Functions of C1-COM and C11-COM for triolein/dioxane (a) and triolein/ GVL (b) binary mixtures. Plotted in solid lines is the density ratios at 333.15K and dotted lines is at 298.15K.

4.3.3.1 Site to site distribution functions

Selected radial distribution functions of the different sites of THF with the polar and non-polar regions of triolein are shown in Figure 32. The closest interactions sites are between O2(triolein)/C1(THF) and O2(triolein)/C4(THF) with both sites showing peaks at about 3.62 Å. These two peaks are strong indicating the importance of these sites in interactions of triolein. The O2(triolein)/C4(THF) indicates that the interaction is probably dipolar. Since the dipole moment vector of THF bisects the oxygen atom and the C3-C4 bond, if the O2(triolein)/C1(THF) peak

was due to the same conformer, it would occur at a significantly longer distance than 3.62 Å, indicating that there is another interaction mode primarily via O2(triolein)/C1(THF). The O2(triolein)/O1(THF) peak at 4.64 Å also cannot be accounted for by this conformer. Another evidence of the existence of multiple THF dispositions towards triolein is the spacing between peaks one and two of O2(triolein)/C4(THF). These two peaks are separated by 1 Å, which is too small to be due to a second solvation shell. The existence of multiple favourable interaction modes of triolein and THF is a strong possibility given that triolein itself occurs in different isomeric forms as will be discussed later. C19(triolein)/C4(THF) and C19(triolein)/C1(THF) peaks are also strong but occur at larger distance of 3.96 and 3.89 Å respectively. As expected, the interaction of the THF oxygen atoms with the non-polar region of triolein is very weak as shown by the C19(triolein)/O1(THF) rdf. In general, all the interactions of triolein via the THF oxygen atom are weak and occur at longer distance (blue lines).

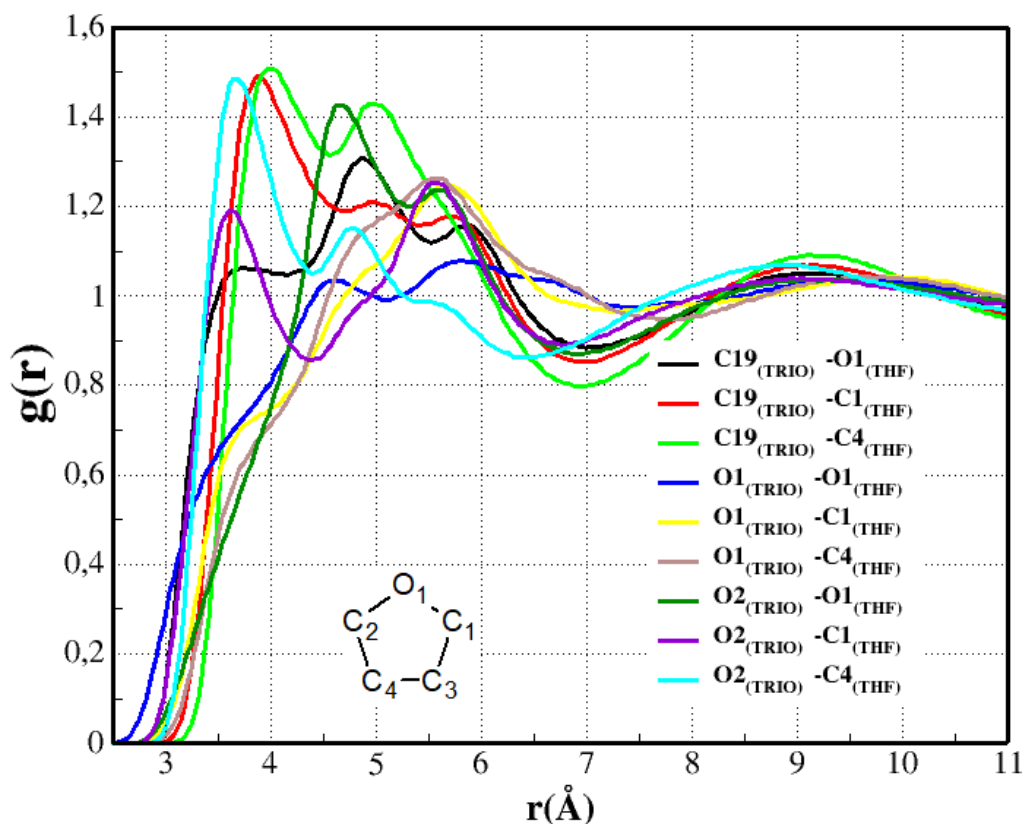


Figure 32: Site to site radial distribution functions for triolein _THF interactions. (Insert is the numbering of THF atoms).

Several site to site radial distribution functions for CPME, a greener solvent more likely to replace THF as an important solvent for biodiesel production were calculated. These are shown in Figure 33. The most prominent peaks are O2(triolein)/C6(CPME) and C19(triolein)/C6(CPME). This shows that CPME interacts with triolein via the methyl group, and it is able to do so strongly at the hydrocarbon part and at the carbonyl oxygen showing strong polar interaction agreeing with the results from Figure 27. The position of ester O1 (triolein) might be hindering interactions as shown by weaker peaks which are also appearing at longer distance as seen in O1(triolein)/C3(CPME), O1(triolein)/C5(CPME) and O1(triolein)/O1(CPME). The O1(triolein)/C6(CPME) appears at 3.8Å, but it is still weak when compared to other interactions involving C6(CPME).

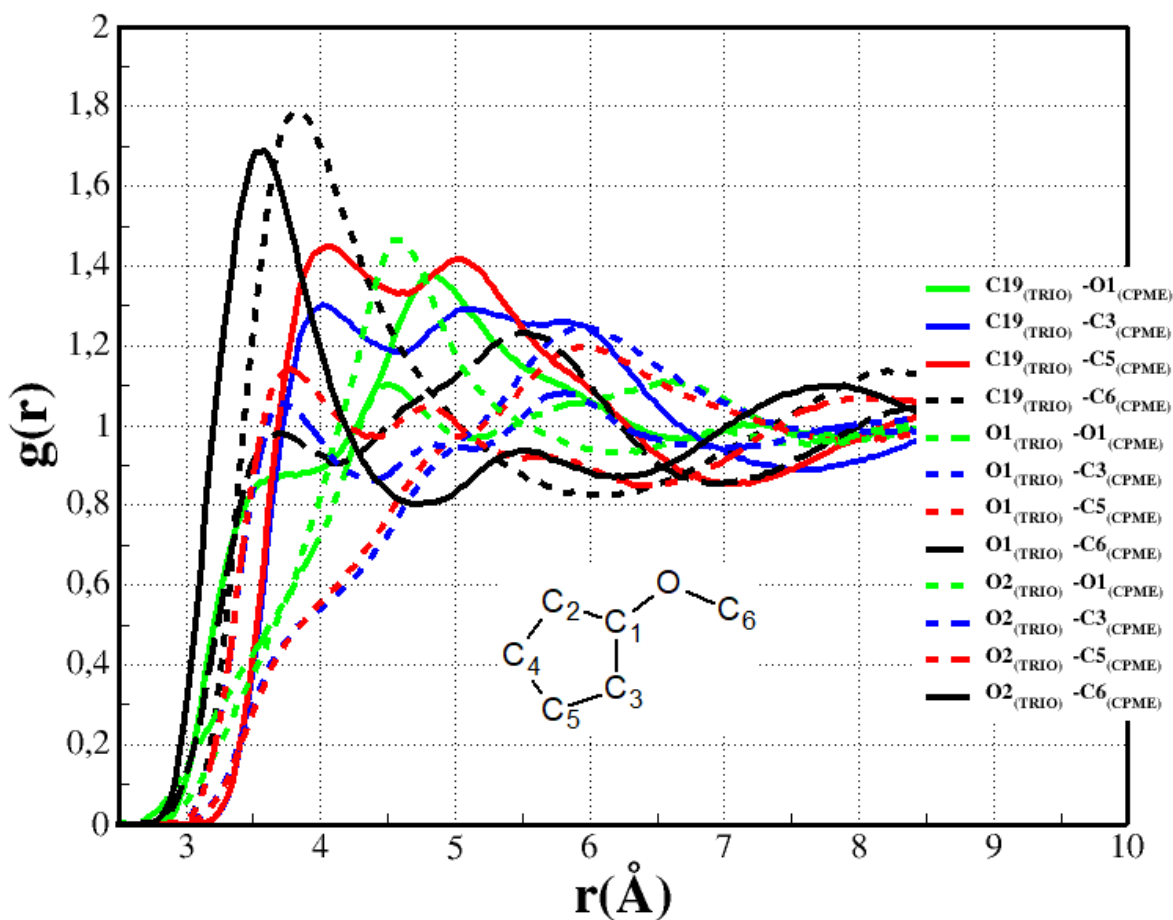


Figure 33: Site to site radial distribution functions for triolein _CPME interactions. (Insert is the numbering of CPME atoms).

The strong interaction between triolein O2 and C19 with the methyl group in CPME may suggest that the CH₃ groups in hexane will interact even more strongly with the triglyceride. In Figure 34, the RDFs of O2(triolein)-C6(CPME) and C19(triolein)-C6(CPME) are compared to O2(triolein)-C6(hexane) and C19(triolein)-C1(hexane) (see insert for numbering of hexane atoms). The first O2/C6 RDF peaks appear at shorter distance in both CPME and hexane than the C19/C6. In both cases the CPME peaks are stronger than the hexane peaks for similar interaction sites and appear at shorter distances. The fact that C6 is bonded to O in CPME might be helping to increase the interaction with triolein. The CPME peak heights do not differ as much compared to the hexane peaks, indicating that CPME distribution around the triolein is more uniform than that of hexane, in agreement with the regional density analysis discussed in section 4.3.2 (See Figure 27(b and d)). These results show the importance of polarization effects in the interaction between triolein and co-solvent, not just with the polar part of triolein, but with the non-polar part as well.

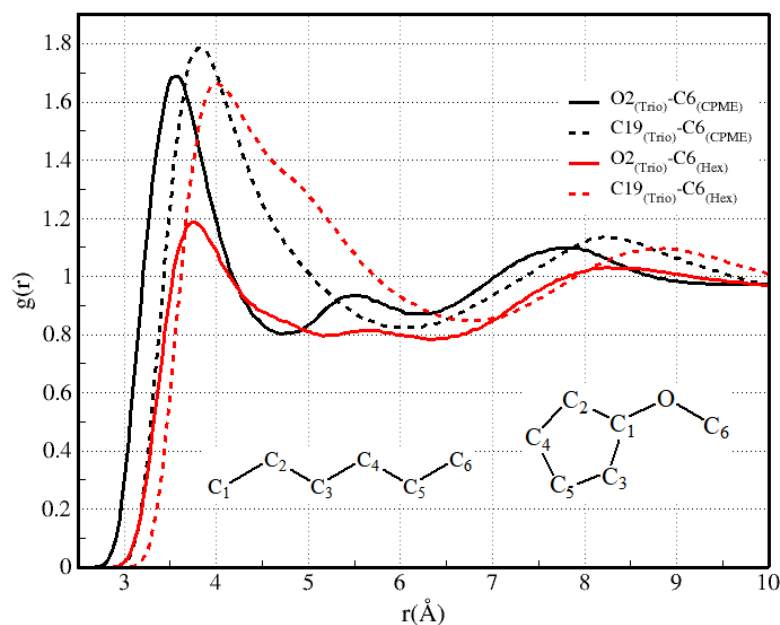


Figure 34: Site to site radial distribution functions for triolein-CPME interactions and triolein-Hexane (C19-C6) and (O2-C6). Insert is the numbering for both CPME, and hexane used in the calculations.

The site to site RDFs for several interaction points between triolein and DEE are shown in Figure 35. The strongest peak observed was between the terminal carbon of triolein and terminal carbon of DEE i.e., C19 (triolein)/C1(DEE). This is not surprising in consideration of both the structure and polarity of diethyl ether which makes it to have strong affinity for the hydrophobic part of triolein [228,229]. DEE also experiences strong interactions to the carbonyl oxygen of triolein (O2) via C4 and O1, although they are weaker when compared to C19 (triolein)/C1(DEE). It must be noted that O2(triolein) /O1(DEE) is observed at a longer distance of 4.7 Å when compared to C19(triolein)/C1(DEE). All the interactions arising from O1(triolein) are the weakest with some of the RDFs not showing any defined peaks. This can be attributed to the location of this interaction point which is not accessible.

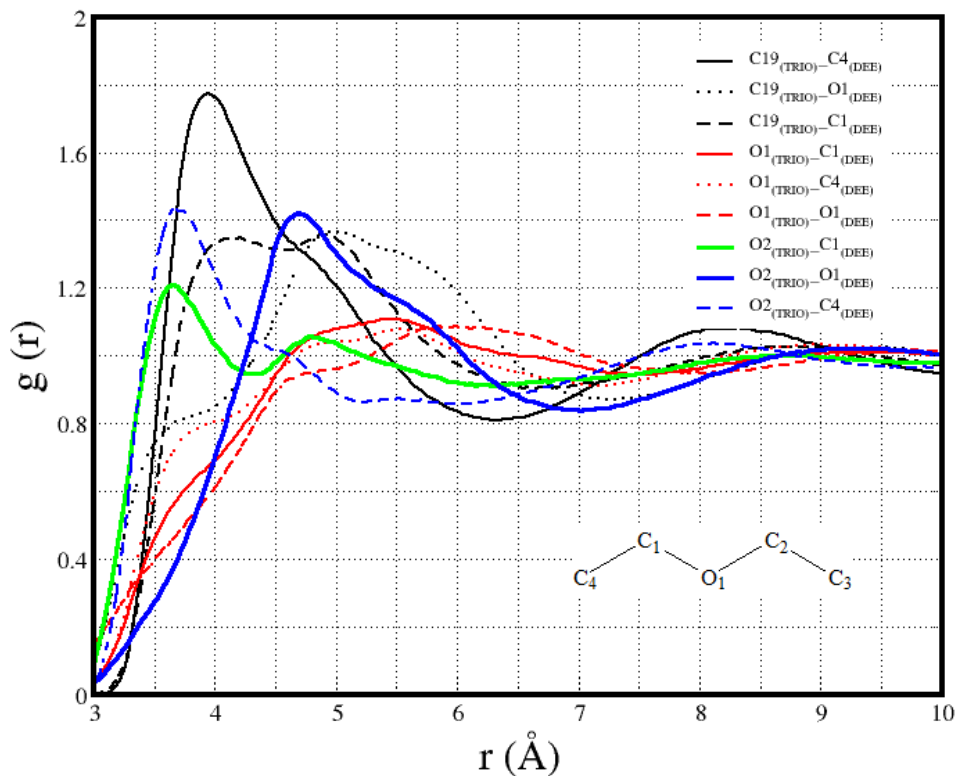


Figure 35: Site to Site radial distribution functions for triolein _DEE interactions. (Insert is the numbering of DEE atoms).

The site to site interactions were also calculated for various interaction points between dioxane and triolein atoms. As shown in Figure 36 the majority of the RDFs peaks are of weaker

intensity, and they do not converge to unity as expected. The strongest peak had an intensity $g(r)$ of only 1.2 and was observed for the interaction between the carbonyl oxygen of triolein and oxygen atom of dioxane, i.e., O2(TRIO) /O1(Dioxane). This peak appears at a longer distance of 4.6 Å. This is followed by C19(TRIO)/C1(Dioxane), O2(TRIO)/C1(Dioxane) and O2(TRIO)/H1(Dioxane) which are still weaker and observed at a much shorter distance of 3.8 Å, 3.5Å and 2.7Å respectively. Dioxane is a solvent that has a much higher density than the other solvents used in this study. It is unique in that it can exist in two different conformations, a chair conformation which is non-polar, and a boat conformation which is polar. The weaker interactions observed between dioxane and triolein could be attributed to the difficulty in accessibility to the interaction point due to different conformers[107,226].

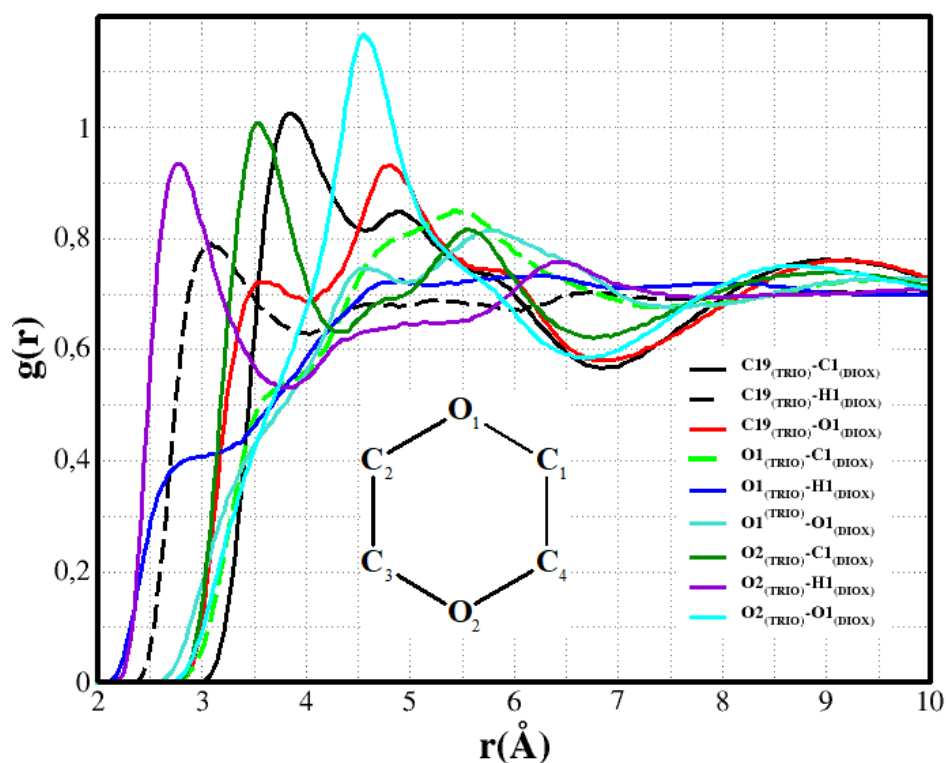


Figure 36: Site to site radial distribution functions for Triolein dioxane interactions. (Insert is the numbering of dioxane atoms).

The strongest atom to atom correlations for triolein and GVL occurs between carbonyl oxygen and methyl carbon, i.e., O2(TRIO)/ C5 (GVL) at a distance of 3.6 Å (Figure 37). This is followed by C19(TRIO)/ C5 (GVL) which also occurs at a slightly longer distance of 3.84 Å, which make

C5 to be a better interaction point when compared to other atoms in GVL molecule. However, it should be noted that all these peaks are very weak, which shows that interactions between GVL and triolein are very weak, and all have $g(r)$ high are less than 1.

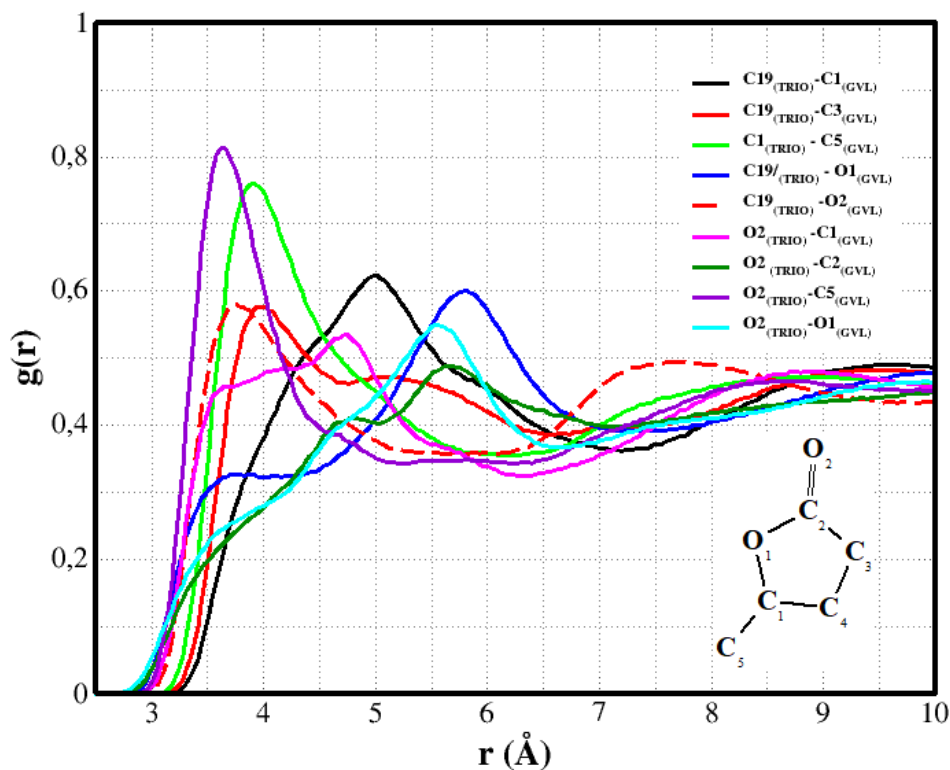


Figure 37: Site to Site radial distribution functions for Triolein GVL interactions. (Insert is the numbering of GVL atoms).

4.3.3.2 Coordination around triolein

Coordination numbers around the first solvation shell, presented in **Error! Reference source not found.**, were calculated from the radial distribution functions C1-COM and C11-COM, according to equation 4.3.

$$N_{AB} = 4\pi\rho_B \int_0^{r_{min}} r^2 g_{AB}(r) dr \quad 4.3$$

Where N_{AB} represents the number of species of A surrounding B in a shell extending from zero to r_{min} (the first minimum in the RDF) and ρ_B is the number density of species B . In both cases the highest coordination numbers are due to CPME/triolein followed closely by THF/triolein. With

the exception of GVL and 1,4-dioxane, higher coordination numbers occur around C11-COM than C1-COM, in agreement with the region-specific analysis discussed in section 4.3.2. The coordination numbers are consistent with cluster size distribution, which was performed as follows. A total of 5000 triolein reference molecules were randomly selected from the molecular dynamics trajectory frames and for each reference triolein molecule, the coordinates of the atoms of the reference triolein itself and those of any other triolein or co-solvent molecule found within the first solvation shells were saved [176]. The solvation shells were based on the radial distribution functions of the solvent centre of mass (COM) about the triolein C1 atom (see Figure 29(a)). The minima in the first solvation shells were found to occur at the following radii of 7.65Å for CPME, 7.24 Å for DEE, 6.67 Å for dioxane, 7.05 Å for THF, 7.86 Å for hexane and 7.43Å for GVL. With this procedure, several clusters were found (Figure 39 and Figure 40). Many of the clusters contained a single triolein molecule and several co-solvent molecules, and for the sake of brevity, our analysis is focused on such clusters, shown in Figure 40. If dissolution or mixing occurs, one might expect to find high occurrences of a single triolein molecule solvated by several co-solvent molecules. From the plots in Figure 40, we see that CPME, DEE, hexane and THF have high occurrences of such clusters, where the number of solvent molecules ranges from 4 to 7. The coordination numbers calculated using RDFs were similar to the most abundant clusters (**Error! Reference source not found.**).

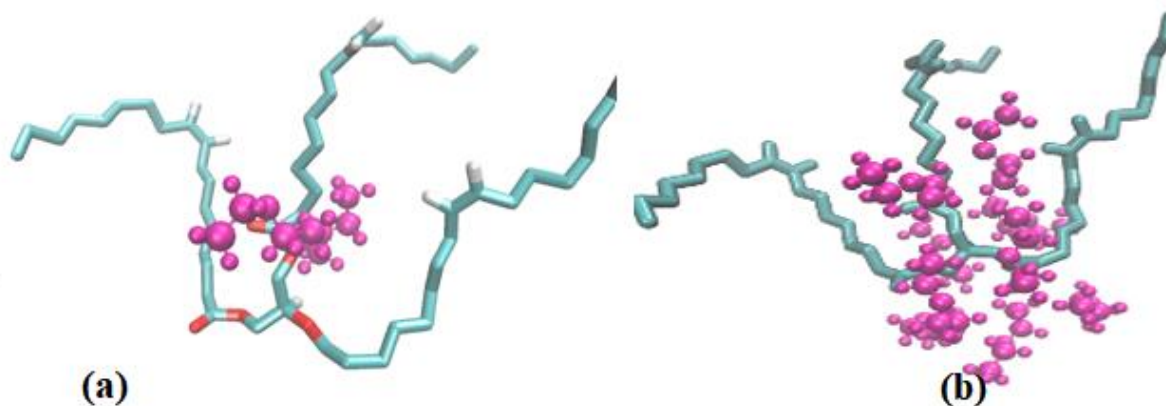


Figure 38: Example of clusters formed between 1 triolein molecule (green) and 2 diethyl ether molecules (purple). (a) shows Trio₁_Dee₂ clusters, while (b) shows Trio₁_Dee₇.

Table 4. 1: Calculated coordination numbers and the most frequently observed cluster (TRIO)_x-(co-solvent)_y cluster

Co-solvent	Calculated coordination numbers (RDFs), C1-COM (co-solvent)	Calculated coordination numbers (RDFs), C11-COM (co-solvent)	Most frequently observed cluster	
			x	y
THF	5.43	6.29	1	6
CPME	6	6.4	1	6
GVL	2.48	2.2	1	1
DIOXANE	3.98	3.88	1	3
DEE	4.98	6.00	1	5
HEXANE	4.12	5.59	1	5

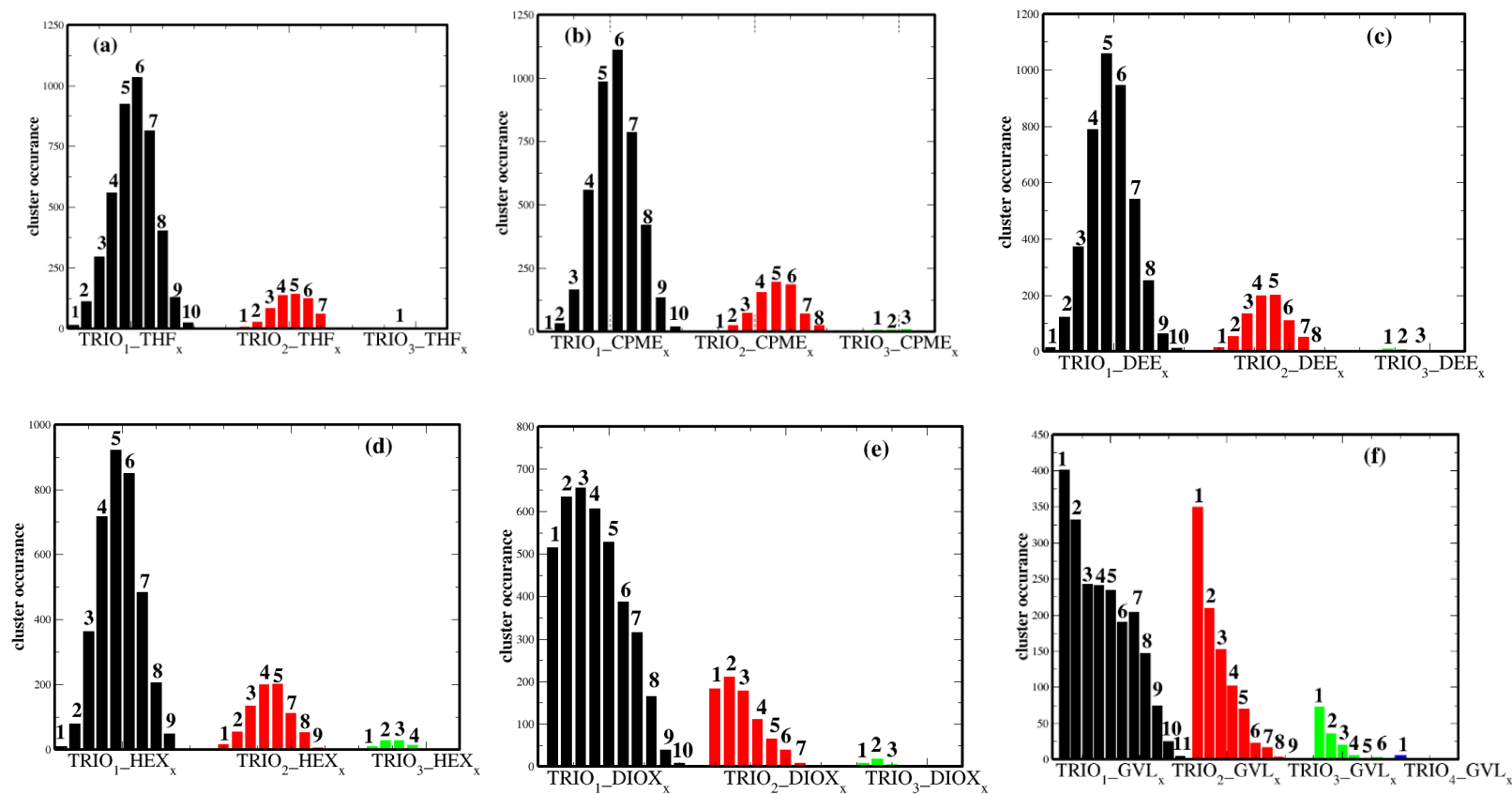


Figure 39: Triolein-solvent cluster distribution within the first coordination shell. (a)-THF, (b)-CPME, (c) DEE, (d) Hexane, (e) Dioxane, (f) GVL and (g) methanol. The x-axis labels the number of triolein molecules in a cluster and the number of solvent molecules is shown in the numbers on top of the bar. For example, the most abundant cluster for Triolein/Methanol is TRIO₁-THF₆

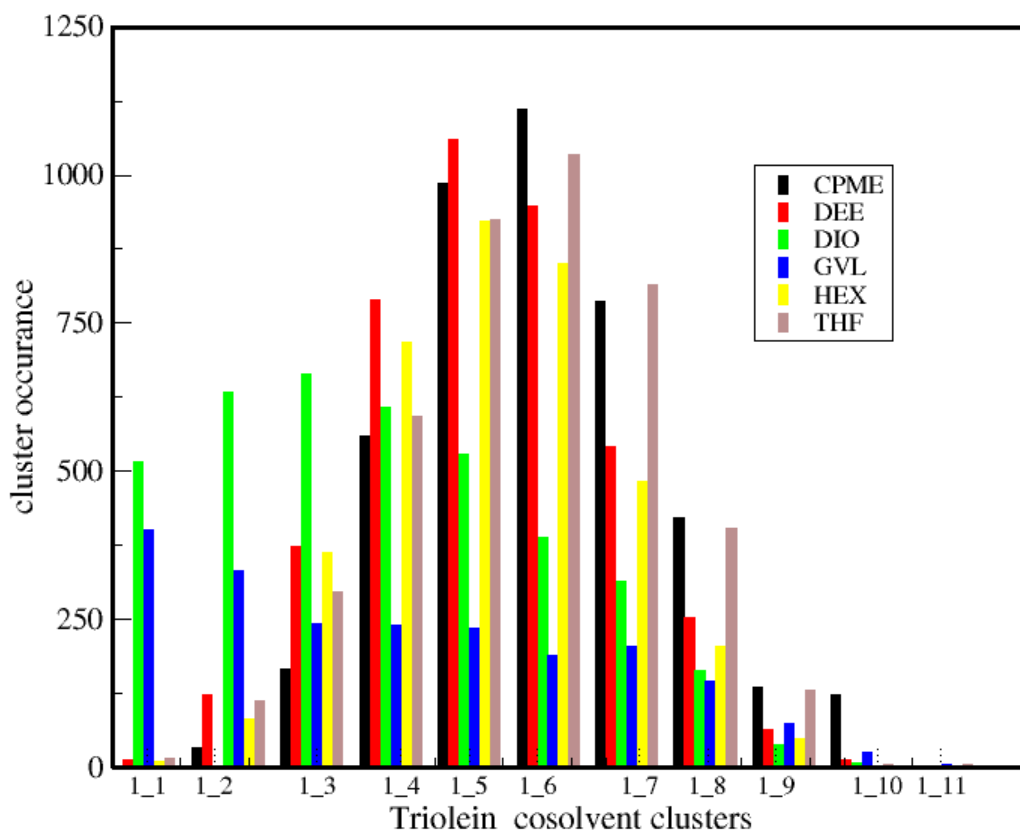


Figure 40: Triolein-co-solvent cluster distribution within the first coordination shell. Triolein is the reference molecule.

4.3.4 Orientation of triolein molecules in pure and solvated triolein

Next, we investigated the effect of solvent molecules on the conformation of triglyceride chains. Based on the relative orientations of the triglyceride chain, the triglyceride conformers can be classified broadly as being shaped like a propeller, a tuning fork, a chair or a trident (see illustrations in Figure 41) [169,174,230]. This classification is based on the angles between three hydrocarbon chains (Figure 42 and

). According to this classification, for a molecule in a propeller conformation the three angles are uniformly distributed around an average value of 120° . In Tuning fork, two opposite chains are pointing in the same direction and the third one in the opposite direction. In chair conformation, two adjacent chains are pointing in the same direction and the third one in the opposite direction. While in the trident conformation, the three chains are pointing in the same direction. Following this classification, the relative amounts of these conformers in both

pure and solvated triolein were calculated, and results are presented in Table 4. 3: Percentage

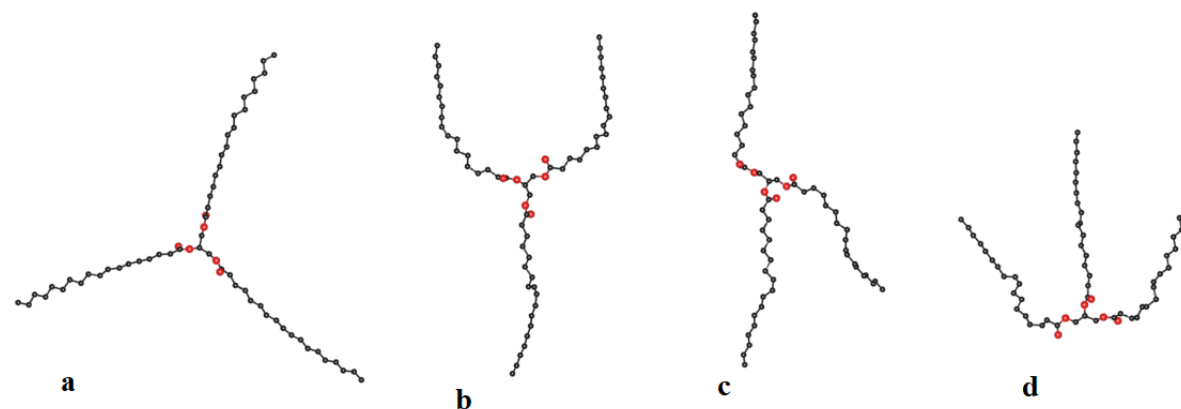


Figure 41: Illustrations of conformation of triolein molecules. (a) Propeller, (b) Tuning fork, (c) chair and (d) Trident.

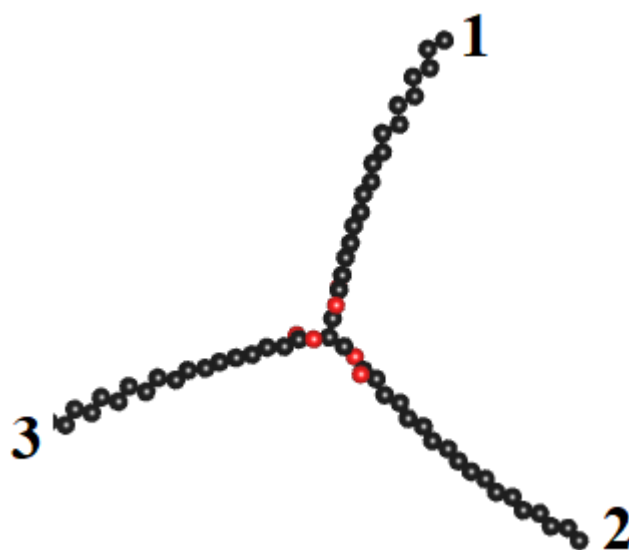


Figure 42: The sketch showing classification of angles. With θ_{12} being an angle between chain 1 and 2, θ_{13} (angle between 1 and 3) and finally θ_{23} is the angle between chain 2 and 3.

Table 4. 2: Criteria for the definition of TG conformations in terms of angles between the chains[169,174].

Conformations	Angles		
Propeller	$75 < \theta_{12} < 165$	$75 < \theta_{23} < 165$	$75 < \theta_{13} < 165$
Tuning fork	$95 < \theta_{12} < 180$	$95 < \theta_{23} < 180$	$0 < \theta_{13} < 75$
Chair	$0 < \theta_{12} < 75$	$95 < \theta_{23} < 180$	$95 < \theta_{13} < 180$
	$95 < \theta_{12} < 180$	$0 < \theta_{23} < 75$	$95 < \theta_{13} < 180$
Trident	Otherwise		

In bulk triolein, the trident and propeller are the most common conformations with the percentage of trident only slightly higher at 28%. Tascini et al. calculated the distribution in pure sebum triglyceride and found the probability of propeller, tuning fork, chair and trident conformers to be 27.73 %, 39.06%, 17.58% and 15.63% respectively[169]. Triolein has longer chains than sebum triglyceride and this could explain the differences in the orientation of the molecules in the bulk. The addition of co-solvent appears to affect the distribution of these conformers. When no solvation occurs (GVL and dioxane), the trident is the predominant conformer, where it appears that the solvent approaches the molecule at the C1, as shown by stronger peaks in the C1-COM RDFs (Figure 31(e-f)). This causes all the hydrocarbon chains to face the opposite side from the solvent, thereby causing trident conformation. This conformation allows the hydrocarbon chains to be closer to each other and harder for solvent molecules to approach and solubilise it. Solvents that are soluble in triolein have high propeller as well as trident conformations (THF, CPME, DEE and Hexane), while those that are only slightly soluble or insoluble have a high composition of trident conformations, as reported in Table 4.3.

Table 4. 3: Percentage of finding different conformers of Triolein molecules in bulk-TG and co-solvent/triolein mixture.

	Bulk Triolein	GVL	HEXANE	Dioxane	THF	CPME	DEE
Propeller	26.70	21.46	28.18	27.42	27.89	28.84	28.18
Tuning Fork	23.04	25.54	21.77	20.7	23.45	21.93	22.44
Chair	22.48	21.91	21.80	21.22	21.80	21.66	20.43
Trident	27.78	31.09	28.25	30.66	26.86	27.57	28.95

4.4 Conclusions

Molecular dynamics simulations were used to study the interaction of triolein and co-solvents with triolein. The calculated density of pure triolein was found to be 911Kg/m^3 (which is very close to the experimental value of 907Kg/m^3). The changes in partial densities across the simulation boxes were also used to investigate the mixing of triolein with co-solvents. It was shown that in the first 10 ns all the systems were biphasic. For miscible systems, the partial densities of solvent and triolein densities gradually become uniform, demonstrating a change from a biphasic system to a single-phase system in the last 10 ns. When mixing is slow, the partial density does not become uniform in the last 10 ns. Preferential solvation was also noticed in different regions of triolein. It was found that some solvents were more attracted to the polar part of triolein, while others were more attracted to the aliphatic part of triolein. The radial distribution functions of carbon 1 of triolein (C1) and solvent centre of mass (COM), C1-COM and carbon at the centre of the aliphatic chain (C11), C11-COM showed the presence of three peaks in decreasing intensity, which is typical of liquids. From these results, the miscibility of the solvents and triolein can be related to the intensity of the first peak, with THF being the most miscible followed by CPME>DEE>hexane, whereas the miscibility of 1,4-dioxane improves with an increase in temperature. The coordination numbers for all systems were obtained by integrating the respective RDFs. The results show that CPME can cluster most around one triolein molecule, followed by THF>DEE>HEX>dioxane and GVL. The presence of co-solvents also influenced the

conformation of triolein molecules. In the presence of solvents that dissolved it, triolein prefers to exist in the propeller conformation, but when there is less or no solvation, it prefers the trident conformation.

CHAPTER 5

Investigation of the thermodynamic properties of triglyceride/methanol mixtures in the presence of cosolvent: A molecular dynamics Study

5.1 INTRODUCTION

In CHAPTER 4 molecular dynamics simulations were used to study interactions between binary solutions of cosolvents and triolein, a triglyceride[231]. Radial distribution functions (RDFs), solvent distributions around triolein molecules, and changes in partial densities were used to help understand the interactions that occur between mixtures of cosolvents and triglycerides. This chapter expands the study to ternary triglycerides/methanol/cosolvent mixtures. The aim is to use thermodynamic parameters derived from molecular dynamic simulations to understand and quantify the miscibility of methanol and triglyceride in the presence of cosolvents from a theoretical point of view. The ternary phase behaviour of oil/methanol/cosolvent have been studied by Boocock et al. [201]. The oils studied included soybean oil, palm oil, coconut oil, and canola oil. The studied cosolvents were diethyl ether (DEE), 1-4 dioxane, di-isopropyl ether, tert-butyl methyl ether, and tetrahydrofuran (THF). Triolein, also known as glyceryl trioleate, is made from a condensation reaction between glycerol and oleic acid. It was selected for this study because oleic acid is the main component of palm oil [53] and the second major component of soybean oil which were both used by Boocock et al.[201]. We selected THF and DEE as cosolvents for our study since they are the most widely used cosolvents in transesterification reactions[53,57,76,102,108].

Several theories have been used to model phase behaviours of liquid mixtures including, Universal Functional Activity Coefficient (UNIFAC)[232], Perturbed Chain-Statistical Associating Fluid theory (PC-SAFT)[233,234], Non-Random Two Liquid model (NRTL)[235], regular solution[236,237], Conductor like screening model for real solvents (COSMO-RS)[238,239] and the Flory Huggins theory[240,241]. Hildebrand developed the regular solution theory, which is used to explain the phase behaviour of small molecule liquid mixtures. The theory helps in constructing a predictive model that determines activity coefficients. According to this theory, the size and shape of similar and unlike molecules are

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comparable and the increase in entropy upon mixing follows the ideal entropic effect. The non-ideality or excess thermodynamic properties arise only from the differences in the intermolecular interactions of different components[242]. Regular solution theory cannot be used in the study of mixtures of triglycerides and methanol which have different structures and massive size differences. The Flory-Huggins theory can be used to model the phase behaviour of liquid mixtures in which the components have substantial differences in shapes and sizes. It was designed for flexible chain like molecules which can be easily placed in a lattice without leaving any vacancies[243]. Triglycerides are flexible molecules with ability to take many conformational forms, which makes them good candidates for application of the Flory-Huggins theory[169,231]. The model triglyceride, triolein, has a molecular weight of 885.432 g/mol which is quite large compared to that of methanol of (32.04 g/mol).

The thermodynamic parameters of the ternary system of triolein/methanol/cosolvent will be derived using the Flory-Huggins theory. This theory has been widely used to study miscibility and phase separation of polymers[244,245], polymers and drugs[246–248]. Both binary and ternary systems' miscibility has been quantified via its application. It starts with a traditional Gibbs equation (equation 5.1).

$$\Delta G^m = \Delta H_m - T\Delta S_m \quad 5.1$$

where ΔH_m is the enthalpy of mixing, ΔS_m is the entropy of mixing and T is temperature. For spontaneous mixing ΔG^m is negative. The entropy ΔS_m , is then derived using statistical configurations on the polymer chains according to equation 5.2.

$$\Delta S_m = R(-n_i \ln \phi_i - n_j \ln \phi_j) \quad 5.2$$

Where R is the ideal gas constant, n_i and n_j are the number of moles of components i and j respectively, ϕ_i and ϕ_j are volume fractions. Similarly, the enthalpic change due to mixing can be described as a change in interaction energy between the unmixed and mixed states and derived using equation 5.3.

$$\Delta H_m = (n_i N_A) \phi_2 E_{mix}^{ij} \quad 5.3$$

Where N_A is avogadros constant and E_{mix}^{ij} is the mixing energy which is derived according to equation 5.4.

$$E_{mix}^{ij} = \frac{1}{2} [Z_{ij}(E_{ij}) + Z_{ji}(E_{ji}) - Z_{ii}(E_{ii}) - Z_{jj}(E_{jj})] \quad 5.4$$

Here Z_{ij} is a coordination number of i around j . The interaction energy between individual molecules of species i and j is given by E_{ij} . According to the Flory-Huggins theory, the interaction parameter for any two components i and j , χ_{ij} can be calculated from equation 5.5.

$$\chi_{ij} = \frac{E_{mix}^{ij}}{RT} \quad 5.5$$

When the value of χ_{ij} is negative the different components have a more favourable interaction with each other in preference to interacting with similar molecules and would most probably exist in a single phase. The large positive values indicate that the molecules will preferably interact with similar components and that phase separation will most likely occur [247,249]. Its relationship with the enthalpy is given as,

$$\Delta H_m = RTn_i\phi_j \chi_{ij} \quad 5.6$$

The change in free energy of mixing (equation 5.1) can then be rewritten by combination of equations 5.2 and 5.6 to give equation 5.7.

$$\Delta G^m = RT(n_i \ln \phi_i + n_j \ln \phi_j + \chi_{ij} n_i \phi_j) \quad 5.7$$

The Flory-Huggins interaction parameter is used to quantify the favourability of interactions between two components[245,247]. This parameter has been used to study phase behavior, structures of polymer blends and solubilities of drug molecules in polymers and water[250]. χ can be determined both experimentally and computationally. The experimental studies have been performed using techniques such as inverse gas chromatography[251,252], small angle neutron scattering (SANS)[253] and differential scanning calorimetry (DSC) [246,254], turbidity measurements and Raman spectroscopy[255]. Computational calculations have also been used to predict χ , making it possible to determine the miscibility of a given pair of molecules without any wastage of chemicals[252]. Additionally, blend compatibility of polymers that are otherwise difficult to predict experimentally can be studied computationally[256]. χ has been predicted using computational calculations for binary mixtures, ternary mixtures [255,257,258] and even quaternary mixtures[259]. Although the Flory Huggins theory was originally used to study polymer blends it has been used successfully to study other systems in which significant disparity exists between solute and solvent molecules molar volumes, such as in triglycerides and organic solvents[247,260,261].

The interaction energy can be calculated via molecular dynamic simulation[252,262]. In this chapter the interaction energy E_{ij} between components i and j will be estimated as a sum of the van der Waals and the electrostatic interaction energy terms between non-bonded atoms (equation 5.8).

$$E_{ij} = E_{ij}^{vdw} + E_{ij}^{coul} \quad 5.8$$

The van der Waals term is usually approximated using the Lennard-Jones potential model (equation 5.9).

$$E_{ij}^{vdw} = 4\epsilon[(\frac{\sigma}{r_{ij}})^{12} - (\frac{\sigma}{r_{ij}})^6] \quad 5.9$$

Where ϵ is the well depth of the potential energy, r_{ij} is the interatomic distance and σ is the inter-atomic distance corresponding to the minimum in the potential energy [263]. The electrostatic interaction energy can be calculated from the Coulomb law (equation 5.10).

$$E_{ij}^{coul} = \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad 5.10$$

Where ϵ_0 is the vacuum electric permittivity constant and q_i and q_j are the charges of particles i and j respectively, while r_{ij} is the separation distance between the charge centres.

5.2 Computational methods

5.2.1 System preparation

Molecular dynamics studies were carried out to derive thermodynamic mixing parameters of ternary mixtures of triolein/methanol/diethyl ether and triolein/methanol/tetrahydrofuran. The construction of the configurations, the molecular dynamics simulations and analysis were performed using the GROMACS software[156,162,163]. The interactions between the molecules were described by the all atom optimized potentials for liquids simulation (OPLS-AA) force field [264,265]. Force field parameters, including the charges, were obtained from the LigParGen engine[264]. CM1A-LBCC partial charges were used in this study[266]. Initial configurations of the system were constructed by randomly inserting specified numbers of molecules of triolein, cosolvent and methanol (Figure 17) in a cubic box with dimensions of approximately 8 nm. The mixtures were then energy minimized using the steepest descent algorithm, followed by a short 10 ps isothermal isochoric dynamics (NVT) simulation to relax the system to 298.15 K. The molecules were then subjected to isothermal isobaric dynamics (NPT) with T and P set to 298.15 and 1 bar respectively, for 20 ns. The

pressure was controlled through a Parrinello-Rahman barostat[196] with compressibility set to $4.5 \times 10^{-5} \text{ bar}^{-1}$ and a coupling constant of 2 ps. The temperature was controlled with a modified Berendsen thermostat[192,267] with a temperature coupling constant of 0.1 ps. The timestep for the simulations was set to 1 fs. The Verlet cut-off scheme[268,269] was used for the Van der Waals and short-range electrostatic interactions and was kept at a distance of 1.2 nm. Long range electrostatic interactions were computed using the Particle Mesh Ewald algorithm[270,271].

At the end of the production run, a GROMACS rerun was performed over the saved trajectories to calculate, for each frame, the average short range coulombic and Leonard-Jones interaction energies between similar and different species in the ternary mixture. These were then extracted using the GROMACS utility “*gmx energy*”. This procedure results in 12 interaction energy terms, which are reduced to 6 interaction energy terms following equation 5.8. All the images and trajectories were visualized using VMD software[220].

Preliminarily, the suitability of the force field model to reproduce experimental data was evaluated by calculating the densities of the molecule’s triolein, THF, diethyl ether, and methanol at 298.15 K. The calculated densities are in good agreement with experimentally determined values as shown in Table 5. 1. Experimental densities for the mixtures under study are not available. However, data exists for the related methyl decanoate/1-butanol binary mixtures. Plotted in Figure 43 is the variation of densities of binary mixtures of methyl decanoate and 1-butanol as a function of the mole fraction of methyl decanoate. There is close agreement between GROMACS OPLS-AA calculated densities (black line) and experimental results (red line)[272]. The calculated density of pure methyl decanoate is 0.8753 g/cm^3 while that of 1-butanol was 0.7981 g/cm^3 . The experimental values of the two are 0.8682 g/cm^3 and 0.80576 g/cm^3 respectively [272]. The percentage error in the calculated densities is 0.8166 % and 0.9506 % respectively.

Table 5. 1: Experimental and calculated density of pure liquids used in this study. Both experimental and theoretical data were obtained at 298.15 K.

	Calculated density (g/cm^3)	Experimental Density (g/cm^3)	% error
Triolein	0.9109	0.9078[80,273]	0.3415
Diethyl ether	0.723	0.7135[274]	1.3281
Tetrahydrofuran	0.8765	0.8876[78]	1.2505
Methanol	0.7793	0.7895[273]	1.6035

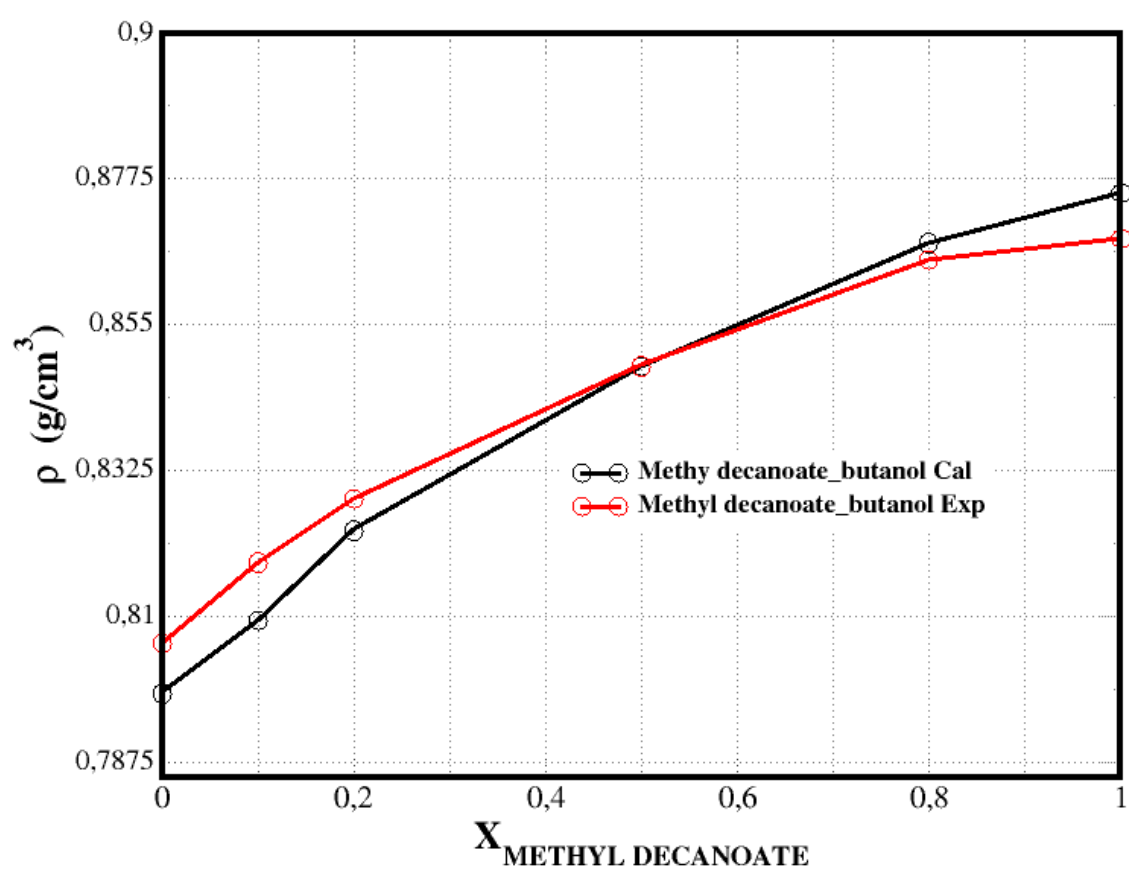


Figure 43: Variation of densities of the mixtures of methyl decanoate and butanol with the mole fraction of methyl decanoate. Both experimental and MD values calculated with OPLS-AA force field. Experimental densities are from reference [272].

5.2.2 Theory and treatment of data for triolein/cosolvent/methanol mixture

The Gibbs free energy for a ternary mixture can be calculated from the expanded equation 5.7.

$$\frac{\Delta G}{N K_B T} = x_1 \ln \phi_1 + x_2 \ln \phi_2 + x_3 \ln \phi_3 + (\chi_{12} \phi_1 \phi_2 + \chi_{13} \phi_1 \phi_3 + \chi_{23} \phi_2 \phi_3)(m_1 x_1 + m_2 x_2 + m_3 x_3) \quad 5.11$$

Where x_i is the mole fraction of component i (1 being triolein, 2 methanol and 3 is cosolvent which is either DEE or THF), K_B is the Boltzmann constant, N is the total number of molecules in the system, ϕ_i s are the volume fractions in the ternary mixture, m_i s are the molar volume ratios referenced to the molar volume of THF or DEE, that is

$$m_i = \frac{V_m(i)}{V_m(THF)} \quad 5.12$$

χ_{12} , χ_{13} and χ_{23} are the binary interaction parameters and can be calculated using equations 5.5 and 5.13 which is the modified version of equation 5.4.

$$E_{mix}^{ij} = \frac{2E_{ij} - E_{ii} - E_{jj}}{2(N_i + N_j)} \quad 5.13$$

E_{ij} , E_{ii} and E_{jj} are the molecular dynamics frame averaged interaction energies between components in the mixture as indexed by the subscripts i and j . Since every possible interaction between species is taken into consideration in calculations of E_{ij}^{vdw} and E_{ij}^{coul} terms by GROMACS, the coordination number Z is implicit in these energies and therefore taken as unity in our case. The chemical potential, μ_i , for each component can be calculated from the partial derivatives of the Gibbs energy using equation 5.14.

$$\frac{\partial \Delta G}{\partial n_1} = \frac{\Delta \mu_1}{RT} = \ln \phi_1 + \left(1 - \frac{m_1}{m_2}\right) \phi_2 + (1 - m_1) \phi_3 + m_1 [\xi_1 (\phi_2 + \phi_3)^2 + \xi_2 \phi_2^2 + \xi_3 \phi_3^2]$$

$$\frac{\partial \Delta G}{\partial n_2} = \frac{\Delta \mu_2}{RT} = \ln \phi_2 + \left(1 - \frac{m_2}{m_1}\right) \phi_1 + (1 - m_2) \phi_3 + m_2 [\xi_2 (\phi_1 + \phi_3)^2 + \xi_1 \phi_1^2 + \xi_3 \phi_3^2]$$

$$\begin{aligned} \frac{\partial \Delta G}{\partial n_3} = \frac{\Delta \mu_3}{RT} &= \ln \phi_3 + \left(1 - \frac{1}{m_1}\right) \phi_1 + \left(1 - \frac{1}{m_2}\right) \phi_2 + \xi_3 (\phi_1 + \phi_3)^2 + \xi_1 \phi_1^2 \\ &\quad + \xi_2 \phi_2^2 \end{aligned}$$

5.14

Where ξ_i is defined as,

$$\begin{aligned}\xi_1 &= 0.5(\chi_{12} + \chi_{13} - \chi_{23}) \\ \xi_2 &= 0.5(\chi_{12} + \chi_{23} - \chi_{13}) \\ \xi_3 &= 0.5(\chi_{13} + \chi_{23} - \chi_{12})\end{aligned}\tag{5.15}$$

At the phase boundaries, the chemical potentials of the ternary mixture must satisfy the following conditions.

$$\begin{aligned}\mu'_1 &= \mu''_1 \\ \mu'_2 &= \mu''_2 \\ \mu'_3 &= \mu''_3\end{aligned}\tag{5.16}$$

Where the single and double prime refers to the oil rich and oil lean phases respectively.

5.3 Results and discussion

Using oil/methanol/THF or oil/methanol/DEE phase boundary compositions from Boocock et al. [201], (Figure 44), the binary interaction parameters (χ_{ij}), Gibbs energy (ΔG_m) and chemical potential μ_i at each data point were calculated and the results are presented in Table 5. 2 for THF and Table 5. 3 for DEE.

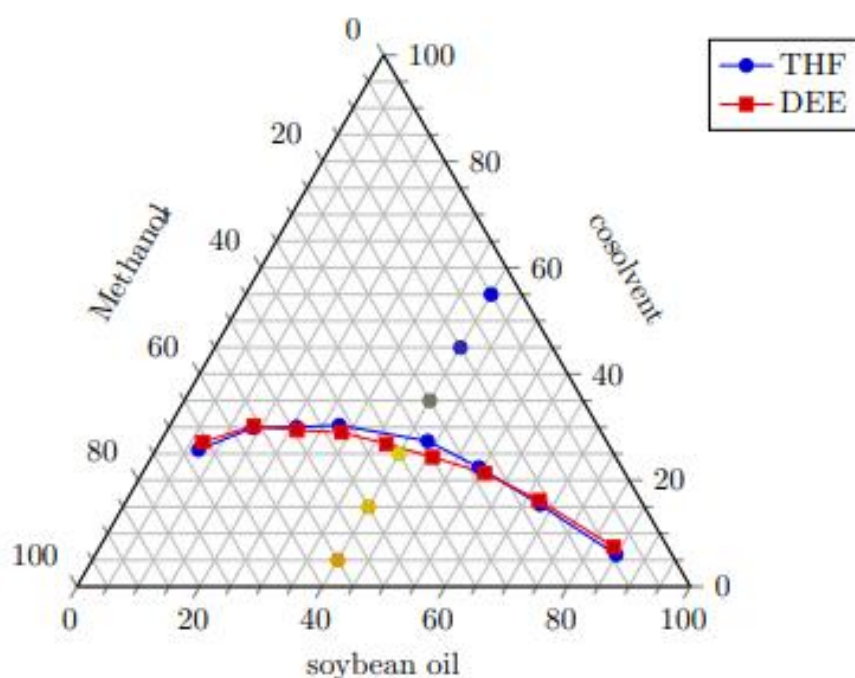


Figure 44: The ternary phase diagram of soybean oil/methanol/THF (blue) and soybean oil/methanol/DEE (red) for regions with fixed volume fraction of triolein ($\phi_{TRIO} = 0.40$). Adapted with permission from Boocock, D. G. B.; Konar, S. K.; Sidi, H. Phase Diagrams for Oil/Methanol/Ether Mixtures. *J. Am. Oil Chem. Soc.* **1996**, 7(10), 1247–1251]. Copyright 1996, John Wiley and Sons[201].

5.3.1 Contribution of van der Waals and electrostatic energy towards the Interaction Energy

The total interaction energy of the system at each volume fraction was calculated from the summation of Lennard Jones (6-12 interaction energy) and electrostatic interactions using equation 5.8. E_{vdw} and E_{Coul} for mixtures of compositions along the phase boundary based on the results from Boocock et al. [201] for systems with THF and DEE are presented in Figure 45(a-d). The highest E_{vdw} values (absolute) are due to triolein-triolein self-interaction, and these increase with an increase with the volume fraction of triolein. This is not surprising considering the huge difference in molecular volume between solvents (methanol, cosolvent) and triglyceride[227]. The van der Waals attractions between the three alkyl chains in each molecule are dominant compared to the cross interactions [275]. The E_{vdw} for triolein-methanol and triolein-THF experiences a slight increase as the composition of triolein increases until $\phi_{TRIO} > 0.6$ where it starts slightly decreasing. It must be noted that these energies are still negative indicative of the strong affinity of these molecules to each other.

The E_{vdw} of methanol-methanol which is showing a slight repulsive behaviour by becoming less negative as the ϕ_{TRIO} increases. The addition of THF or DEE causes a disruption in the strong hydrogen bonding between methanol molecules, which then enhances the triolein-methanol interaction [227]. In both ternary systems, the energy due to electrostatic interactions, E_{Coul} values, for methanol-methanol self-interactions are becoming less negative as the ϕ_{TRIO} increases. This is more noticeable in the system with THF (Figure 45(c)) than the one with DEE (Figure 45(d)). The other noticeable difference is the change in E_{Coul} for cosolvent-cosolvent interactions, which is becoming more positive with increase ϕ_{TRIO} . The DEE-DEE shows lower repulsive interactions than THF-THF. The self-interaction terms in triolein (black curves) seems to dominate all other interactions as the volume fraction of triolein increases.

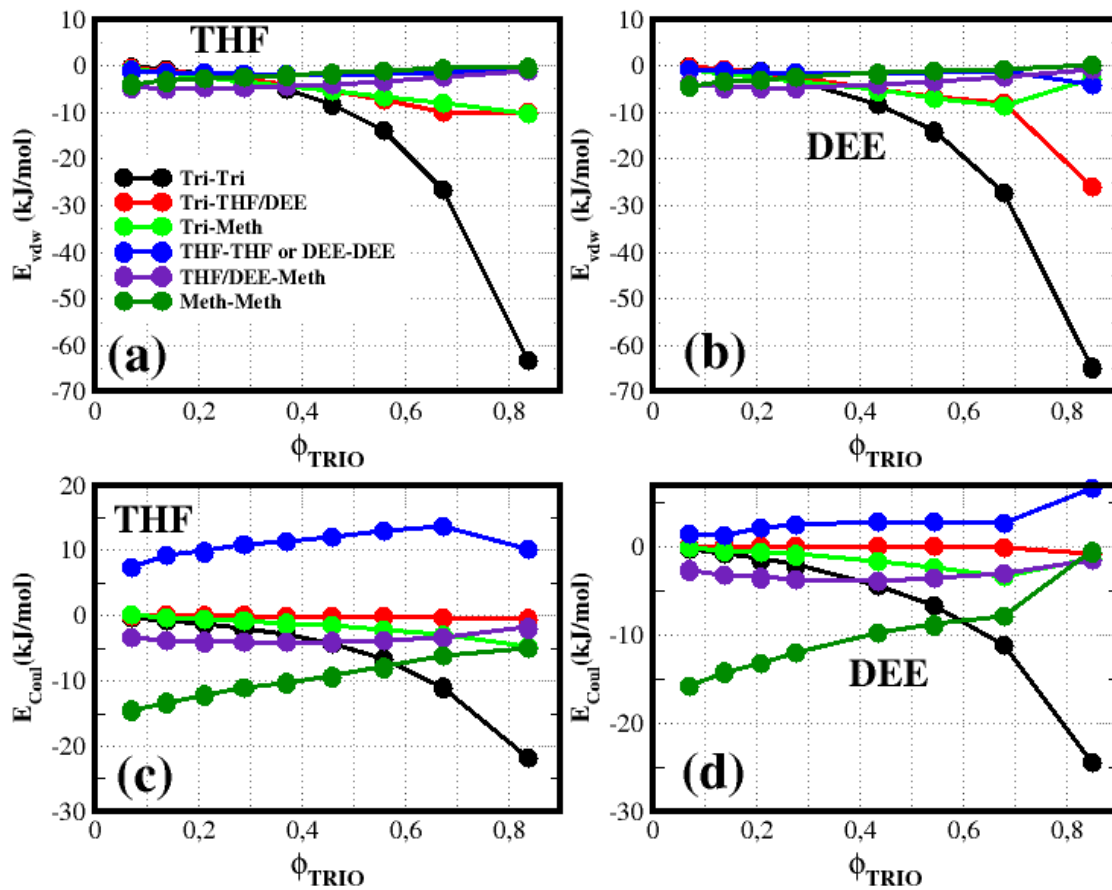


Figure 45: The change in the van der Waals energy (a & b) and the electrostatic energy (c & d) along the phase boundary for a ternary mixture shown in Figure 45 (a & c) is for triolein/methanol/THF while (b and d) is for triolein/methanol/DEE mixture.

Table 5. 2: Summary of χ_{ij} , $\Delta\mu_i$ and Gibbs energy calculated along the phase boundary of experimental results of Boocock et al.[201]. 1=triolein, 2=methanol and, 3 =THF

ϕ_{TRIO}	ϕ_{METH}	ϕ_{THF}	χ_{12}	χ_{13}	χ_{23}	$\frac{\Delta G^m}{RT}$	ΔH_m	ΔS_m	$\Delta\mu_1$	$\Delta\mu_2$	$\Delta\mu_3$
0.069	0.659	0.272	4.148	-7.577	-0.758	-0.633	-0.054	-0.579	-11.724	-0.126	-2.855
0.137	0.561	0.302	3.624	-7.398	-1.855	-0.957	-0.238	-0.719	-16.620	-0.158	-3.344
0.212	0.494	0.294	3.129	-7.483	-2.219	-1.182	-0.353	-0.830	-18.614	-0.123	-3.730
0.286	0.424	0.290	2.799	-7.214	-2.716	-1.474	-0.510	-0.963	-17.958	-0.135	-4.032
0.370	0.361	0.269	2.517	-6.700	-2.962	-1.696	-0.603	-1.094	-15.627	-0.155	-4.264
0.458	0.299	0.243	2.635	-5.407	-3.223	-1.787	-0.541	-1.245	-11.011	-0.201	-4.253
0.558	0.228	0.214	3.346	-3.315	-3.574	-1.639	-0.198	-1.441	-5.810	-0.213	-3.789
0.672	0.166	0.162	6.594	2.268	-3.838	-0.095	1.602	-1.698	0.669	0.362	-1.204
0.837	0.088	0.075	15.88	24.678	-2.756	6.413	8.392	-1.979	3.541	3.563	15.79

Table 5. 3: Summary of χ_{ij} , $\Delta\mu_i$ and Gibbs energy calculated along the phase boundary of experimental results of Boocock et al.[201]. 1=triolein, 2=methanol and, 3 =DEE

ϕ_{TRIO}	ϕ_{METH}	ϕ_{DEE}	χ_{12}	χ_{13}	χ_{23}	$\frac{\Delta G^m}{RT}$	ΔH_m	ΔS_m	$\Delta\mu_1$	$\Delta\mu_2$	$\Delta\mu_3$
0.069	0.673	0.257	4.332	-1.076	1.257	-0.315	0.209	-0.523	0.652	-0.086	-1.977
0.138	0.563	0.299	3.739	-0.879	0.259	-0.524	0.168	-0.692	-2.981	-0.145	-2.238
0.208	0.492	0.300	3.314	-0.707	-0.152	-0.644	0.172	-0.813	-4.7091	-0.183	-2.282
0.276	0.421	0.304	2.908	-0.641	-0.616	-0.800	0.145	-0.945	-5.822	-0.257	-2.245
0.435	0.291	0.274	2.821	1.183	-1.214	-0.856	0.377	-1.233	-2.875	-0.458	-1.604
0.543	0.233	0.224	3.307	4.766	-1.156	-0.345	1.068	-1.413	0.572	-0.568	0.011
0.677	0.168	0.154	6.034	17.968	-0.845	2.215	3.865	-1.650	6.121	-0.490	7.955
0.849	0.091	0.060	18.31	42.81	-1.624	7.580	9.517	-1.939	3.643	3.446	29.84

5.3.2 Binary interactions

The interaction parameters along the phase boundary as shown in Figure 44 are depicted in Figure 46(a and b). Although χ is usually approximated as being independent of composition, several publications have shown that this is not necessarily the case[254,276,277]. As depicted in Figure 46, χ values are clearly solvent dependent. Figure 46(a) shows that when the volume fraction of triolein increases, the binary interaction parameters, χ_{ij} , decrease until around $\phi_{TRIO} = 0.5$ where the values start increasing with ϕ_{TRIO} . The most favorable interactions between triolein and methanol occur at the maximum concentration of THF while the most favorable interactions in triolein/methanol/THF mixtures are those between triolein and THF at low to medium ϕ_{TRIO} , and between methanol and THF at high values of

ϕ_{TRIO} . This is not surprising because of the aprotic nature of THF [225] which enables it to interact strongly with the polar and non-polar parts of triolein[231]. The interactions between methanol and THF as indicated by values of χ_{23} (Figure 46(a) green line)) is largely unaffected by the amount of triolein along the phase boundary. Except for χ_{23} , at ϕ_{TRIO} greater than 0.5 all binary interactions start increasing showing that unfavorable interaction is taking place and repulsive forces are more than the attractive forces. This behavior is more prominent in χ_{13} and χ_{12} . The large values of χ_{13} and χ_{12} at $\phi_{TRIO} = 0.837$ potentially suggest less miscibility between triolein and the two solvents at this volume ratio. In Figure 47, we compare the snapshots of the final and initial configurations of mixtures having low values of χ_{13} and χ_{12} ($\phi_{TRIO} = 0.458$) and mixtures having high values of χ_{13} and χ_{12} ($\phi_{TRIO} = 0.837$). Snapshots of the initial configurations after preparation and minimization stage (before equilibration), (Figure 47(a)), appear homogenous because the particles are inserted into the simulation box randomly. The snapshot of the final configuration of the $\phi_{TRIO} = 0.458$ clearly shows that homogeneity is maintained after equilibration. However, for the $\phi_{TRIO} = 0.837$ aggregation of methanol and THF into large clusters is clearly noticeable after 20 ns. This obviously leads to less interaction between triolein and the two solvents.

The triolein/methanol/DEE system exhibits the same interaction parameters trend as the triolein/methanol/THF system (Figure 46(b), Table 5. 3). However, the interaction parameters obtained for interactions between DEE and triolein (χ_{13}) are less negative than those obtained for THF/triolein at all compositions showing that triolein interacts more strongly with THF than with DEE due to THF's slightly higher dipole moment and dielectric constant which enables it to interact with both ester and aliphatic moiety of triglycerides resulting in stronger interactions[229,278]. The point at $\phi_{TRIO} \approx 0.8$, χ_{13} is higher showing high possibility of unmixing caused by stronger self-interactions overpowering weak intermolecular interactions as a result of high triolein composition, which is similar to what was observed in Figure 46(a) [279].

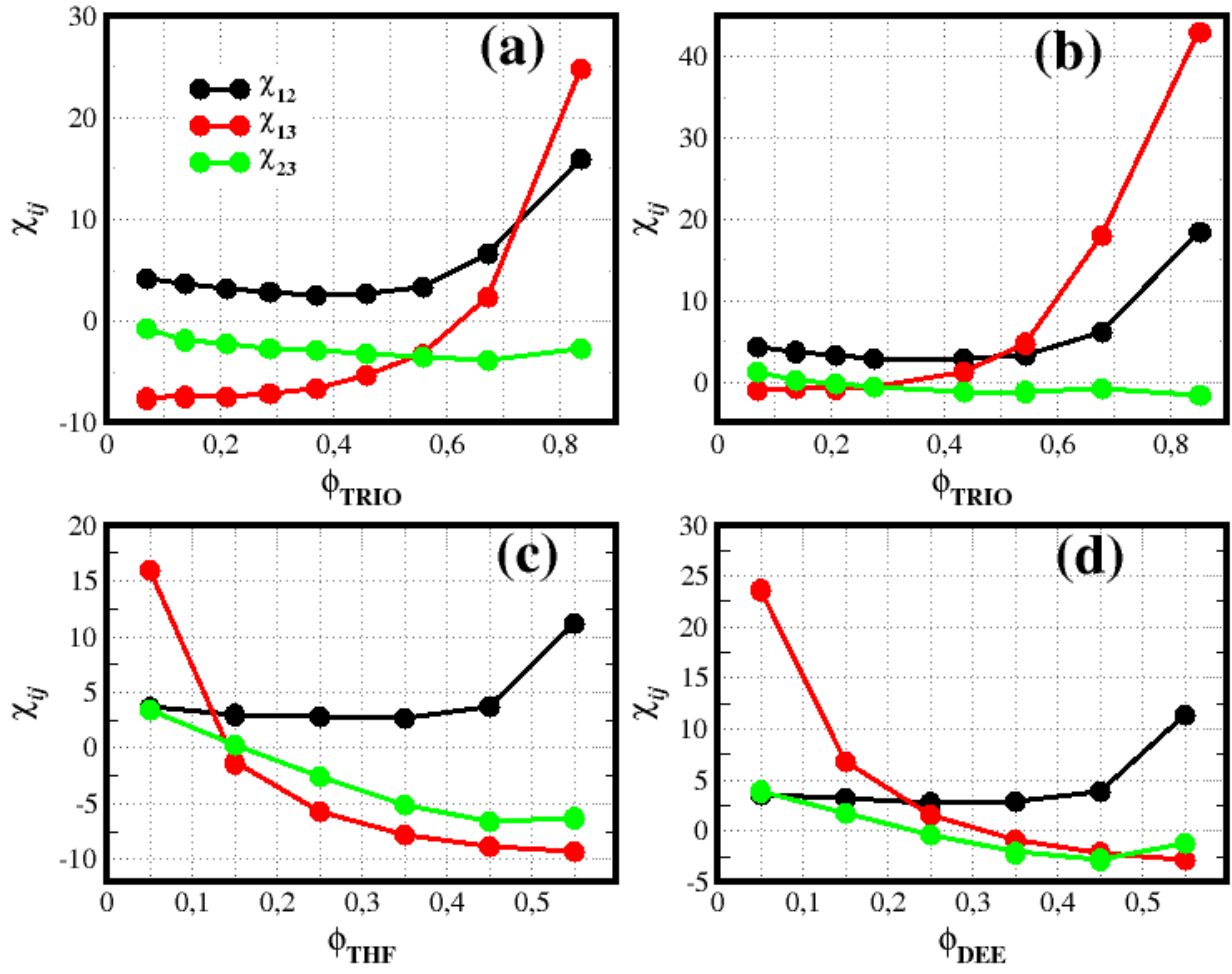


Figure 46: Calculated interaction parameters along the experimental phase boundaries of reference[201] (a) for triolein/methanol/THF and (b) triolein/methanol/DEE ternary mixture and along fixed $\phi_{TRIO} = 0.40$ (c) system with THF and (d) system with DEE.

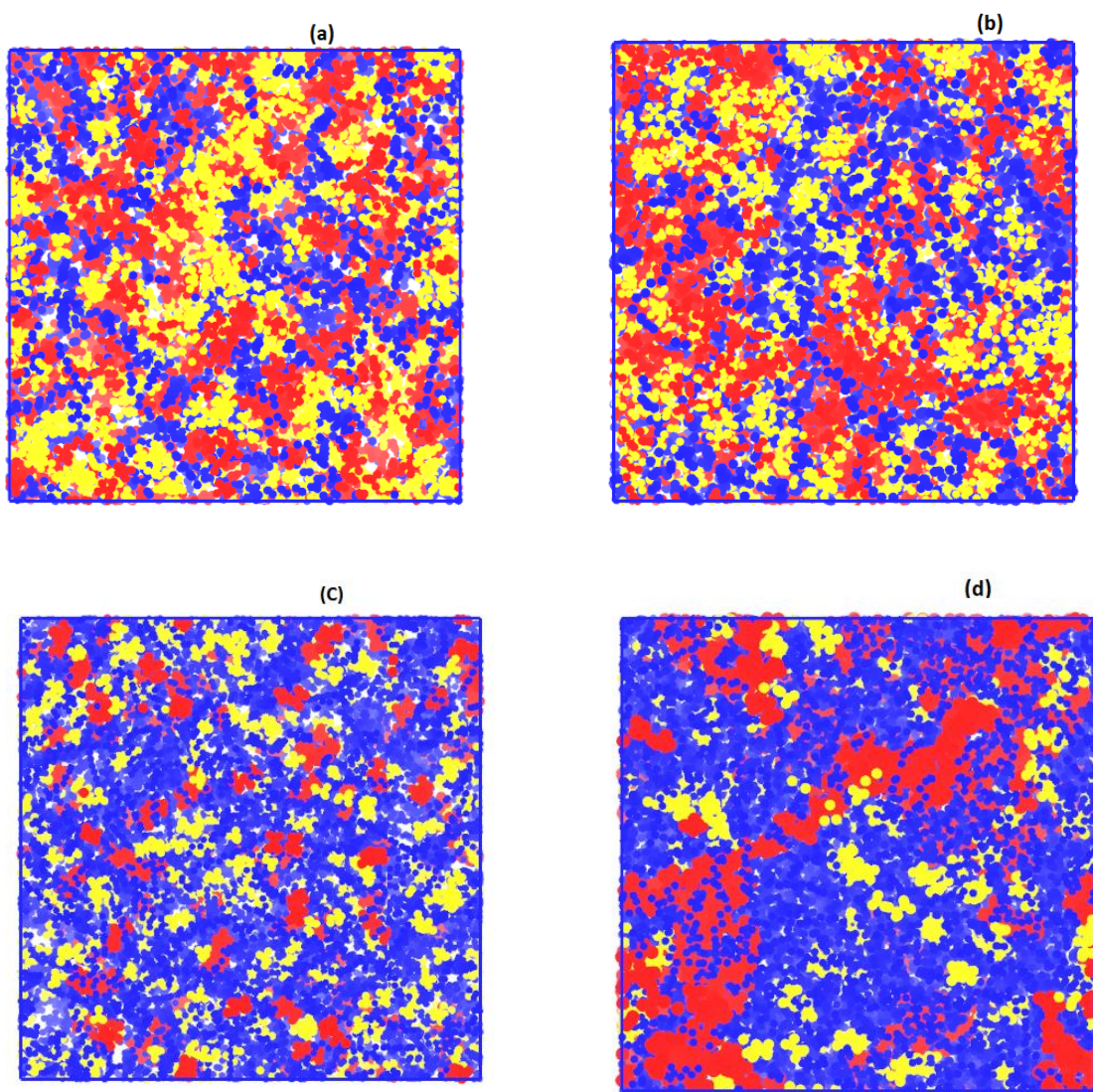


Figure 47: (a) Snapshot of initial configurations for $\phi_{TRIO} \approx 0.458$ along the experimental phase boundary showing homogenous mixture after random insertion and (b) $\phi_{TRIO} \approx 0.458$ after 20 ns of production run showing even distributions of components. (c) Snapshot of the initial configurations for $\phi_{TRIO} \approx 0.8$ along the experimental phase boundary and (d) is the snapshot of the system after 20ns showing aggregation of components. Key: blue – triolein, yellow – THF and red -methanol.

The binary interaction parameters were also calculated for mixtures with constant triolein composition, $\phi_{TRIO} = 0.4$. Figure 46(c-d) shows the variation of binary interaction parameters with volume fraction of the cosolvent at $\phi_{TRIO} = 0.40$. These compositions encompass both the mixed and unmixed phases on the ternary diagram. The addition of THF does not seem to have a large impact on the interactions between triolein and methanol. However, an increase in THF seems to strengthen methanol-THF and triolein-THF interactions as shown by a decrease in χ_{13} and χ_{23} values. This in turn leads to the dispersal of both methanol and triolein, which eventually leads to the formation of a single phase. Similar trends are observed for the case involving DEE as cosolvent. The decrease could indicate that THF can penetrate the hydrogen bond network of methanol enhancing its interaction with triolein which explains improving interactions. Beyond $\phi_{THF} = 0.35$, it appears that adding more THF appears to be having the opposite effect. Its addition appears to promote self-association which is shown by repulsions in the triolein/methanol interactions. At the same time, χ_{13} is decreasing in the whole range studied. When comparing the interactions between triolein and methanol, it seems that these interactions are independent of the solvent used. However, THF has a stronger interaction with both methanol and triolein, which is shown in Figure 48.

Table 5. 4: Summary of χ_{ij} , $\Delta\mu_i$ and Gibbs energy calculated along the region shown in Figure 5.3 1=Oil, 2=methanol and, 3 =THF

ϕ_{THF}	ϕ_{METH}	ϕ_{TRIO}	χ_{12}	χ_{13}	χ_{23}	$\frac{\Delta G^m}{RT}$	ΔH_m	ΔS_m	$\Delta\mu_1$	$\Delta\mu_2$	$\Delta\mu_3$
0.550	0.050	0.4	11.09	-9.310	-6.296	-3.893	-2.928	-0.966	-38.916	-0.853	-2.322
0.450	0.150	0.4	3.710	-8.863	-6.657	-3.549	-2.323	-1.226	-28.640	-1.132	-3.307
0.350	0.250	0.4	2.634	-7.902	-5.193	-2.702	-1.466	-1.236	-20.253	-0.570	-4.100
0.250	0.350	0.4	2.707	-5.766	-2.656	-1.537	-0.419	-1.119	-12.421	-0.113	-4.207
0.150	0.450	0.4	2.971	-1.346	0.181	-0.526	0.429	-0.955	-4.948	0.033	-2.905
0.050	0.550	0.4	3.585	15.961	3.379	0.304	1.012	-0.708	4.653	0.011	3.863

Table 5. 5: Summary of χ_{ij} , $\Delta\mu_i$ and Gibbs energy calculated along the fixed region shown in Figure 5.3 1=Oil, 2=methanol and, 3 =DEE

ϕ_{TRIO}	ϕ_{METH}	ϕ_{DEE}	χ_{12}	χ_{13}	χ_{23}	$\frac{\Delta G^m}{RT}$	ΔH_m	ΔS_m	$\Delta\mu_1$	$\Delta\mu_2$	$\Delta\mu_3$
0.400	0.050	0.550	11.33	-2.950	-1.214	-1.683	-0.633	-1.050	-12.324	-0.507	-1.132
0.400	0.150	0.450	3.842	-2.185	-2.841	-1.690	-0.402	-1.289	-8.608	-0.973	-1.648
0.400	0.250	0.350	2.823	-0.893	-2.172	-1.277	-0.024	-1.253	-5.561	-0.616	-1.969
0.400	0.350	0.250	2.725	1.444	-0.495	-0.698	0.417	-1.115	-3.190	-0.314	-1.653
0.400	0.450	0.150	3.125	6.746	1.609	-0.111	0.813	-0.924	0.207	-0.154	0.130
0.400	0.550	0.050	3.488	23.635	3.868	0.224	0.910	-0.686	2.686	-0.082	6.781

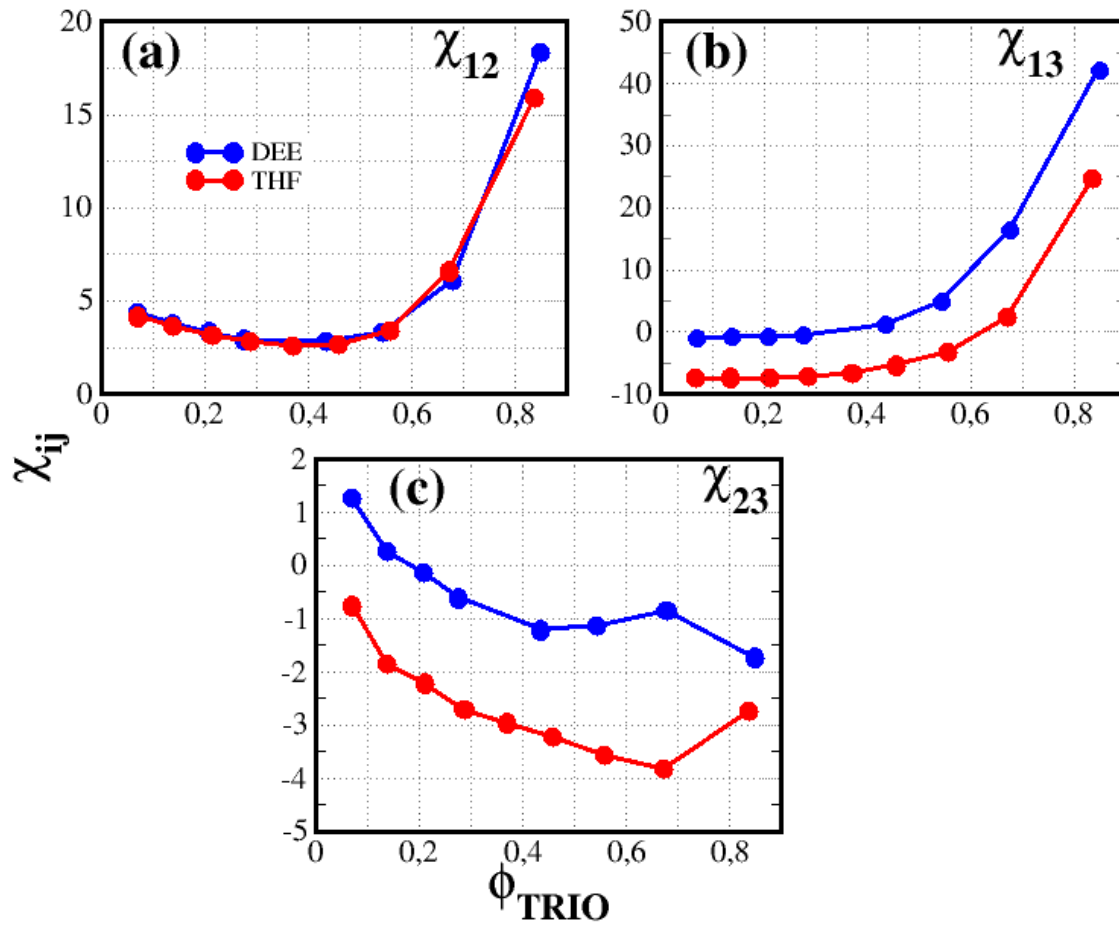


Figure 48: Comparison of binary interaction of systems containing THF and DEE along the phase boundary.

To gain further insight into how the addition of cosolvent affects the structure of triolein and methanol mixtures, the coordination numbers between the two liquids were calculated for the mixtures along the phase boundary. The coordination number, N_{AB} , the number of B molecules around A, is calculated using equation 5.17.

$$N_{AB} = 4\pi\rho_B \int_0^{r_{min}} r^2 g_{AB}(r) dr \quad 5.17$$

Where N_{AB} represents the number of species of A surrounding B in a shell extending from zero to r_{min} (the first minimum in the RDF) and ρ_B is the number density of species B . The radial distribution functions, $g_{AB}(r)$, of the solvent center of mass (COM) around the triolein C1 atom were used to determine these coordination numbers (Figure 49). Presented in Figure 50 is the variation of coordination number (CN) of methanol around triolein molecules as the volume fraction of triolein increases. A gradual decrease in the CN can be observed. This demonstrates that the clustering of methanol around triolein molecules decreases as the volume fraction of triolein increases[176]. Clustering is lowest in areas where self-association is assumed to be strongest in both systems.

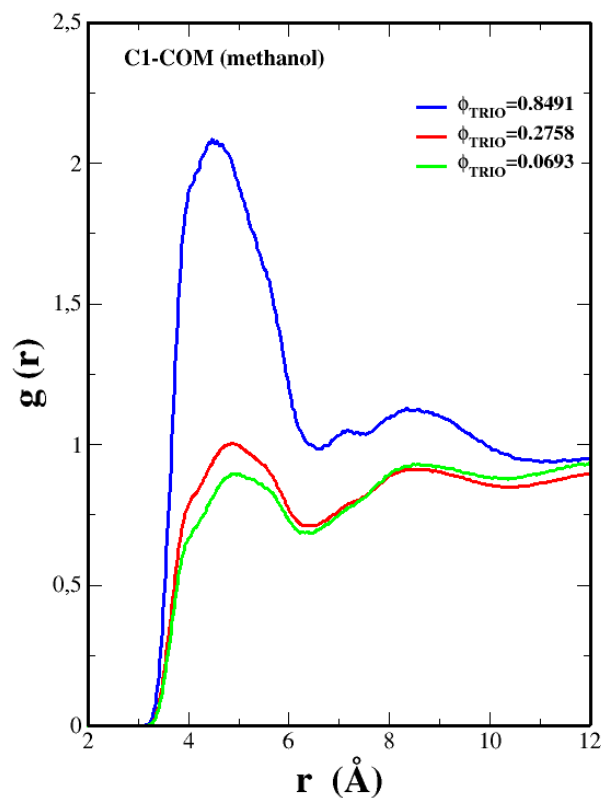


Figure 49: Radial distribution function (RDF) between C1-Triolein and centre of mass of methanol.

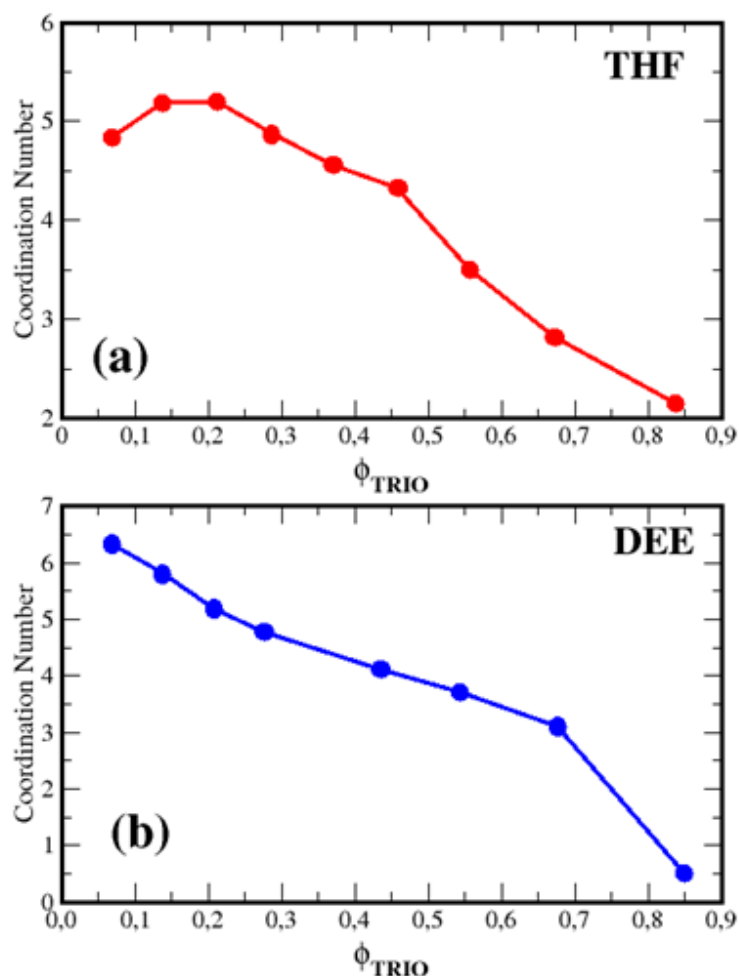


Figure 50: The change in coordination number of methanol around triolein along the phase boundary plotted as a function of ϕ_{TRIO} . (a) triolein/methanol/THF and (b) triolein/methanol/DEE ternary systems.

Another evidence of the predominance of self-association in mixtures with high triolein content, i.e., $\phi_{TRIO} > 0.5$ is via triolein-methanol cluster size distribution. Following the method previously presented in our earlier works[176,231], for single phase systems, there is a high occurrence of multiple methanol molecules clustering around a triolein molecule, with the maximum occurrence observed ranging between 3-7 methanol molecules (Figure 51 and Figure 52). However, when there is aggregation of methanol, non-solvated triolein is abundant. We calculated the percentage of non-solvated triolein molecules, and the results are presented in Figure 53(a & b). In single phase compositions, the percentage of free triolein is very low, but where there is phase separation i.e., $\phi_{TRIO} > 0.65$, the occurrence of free triolein is very high, with the highest occurrence at the highest ϕ_{TRIO} in both systems.

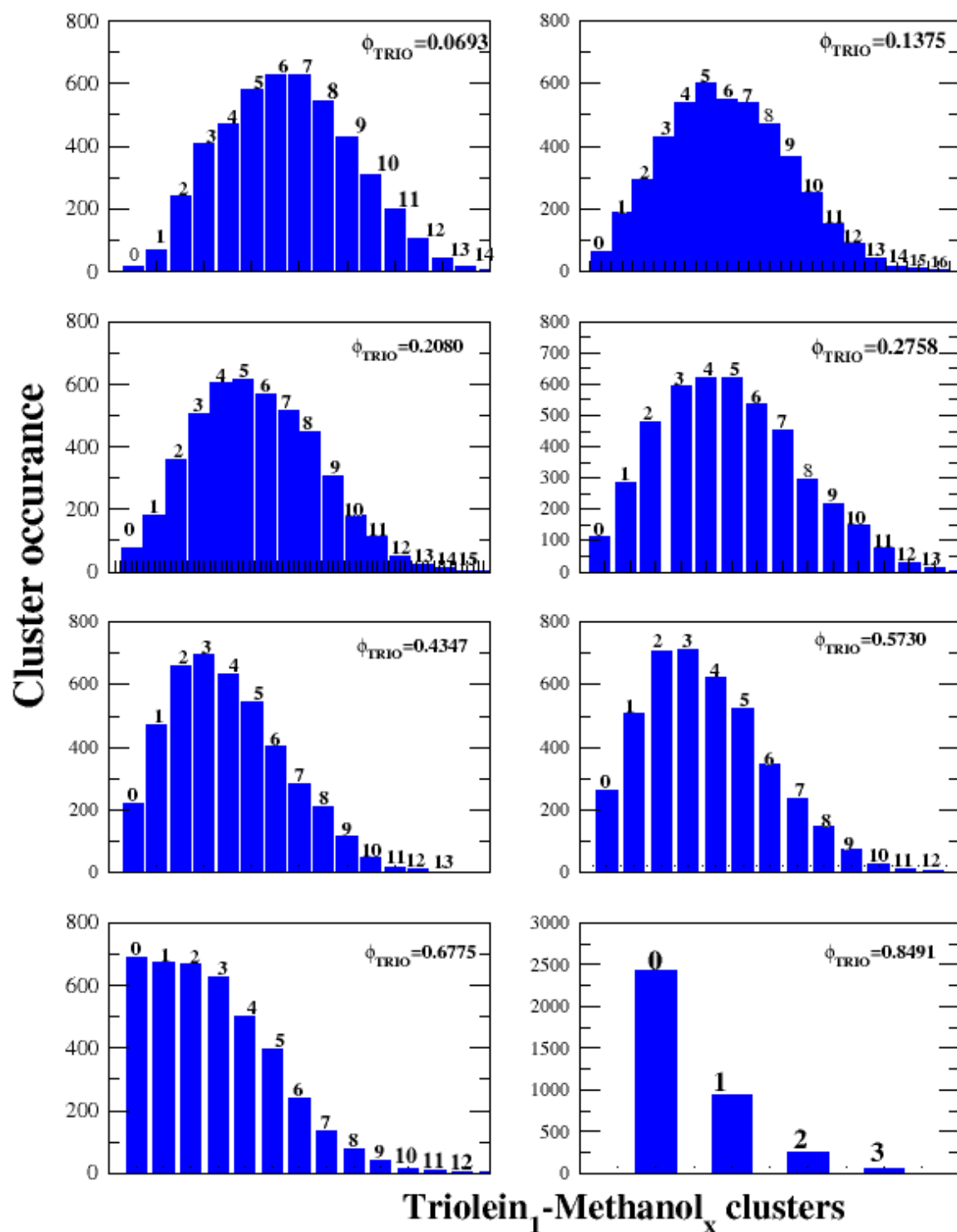


Figure 51: Distribution of triolein-methanol clusters within the first coordination shell. The number of methanol molecules is shown in the numbers at the top of the bar. Data presented here is only for methanol clustering around one triolein molecule, in a ternary mixture of triolein/methanol/DEE.

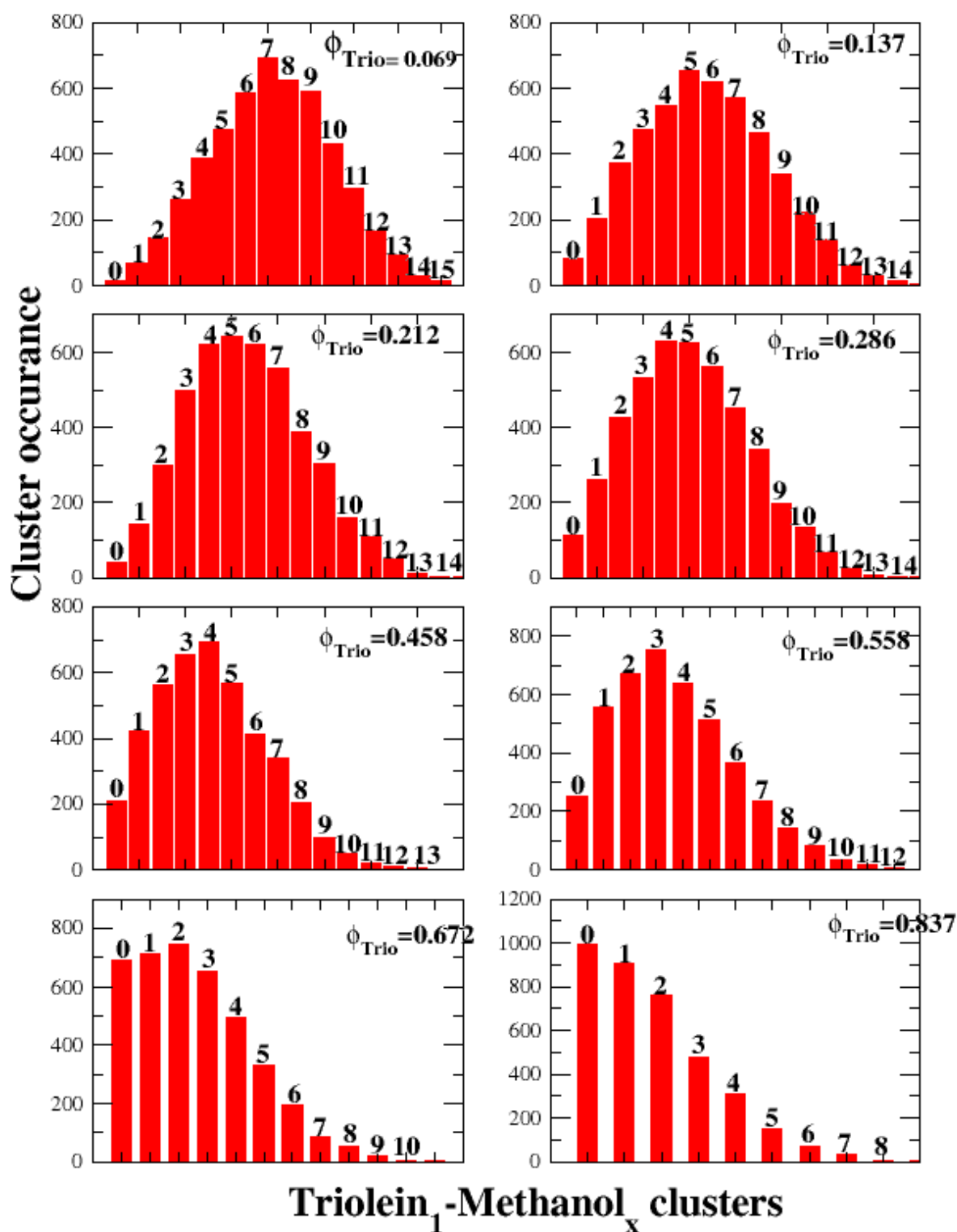


Figure 52: Distribution of triolein-methanol clusters within the first coordination shell. The number of methanol molecules is shown in the numbers at the top of the bar. Data presented here is only for methanol clustering around one triolein molecule, in a ternary mixture of triolein/methanol/THF.

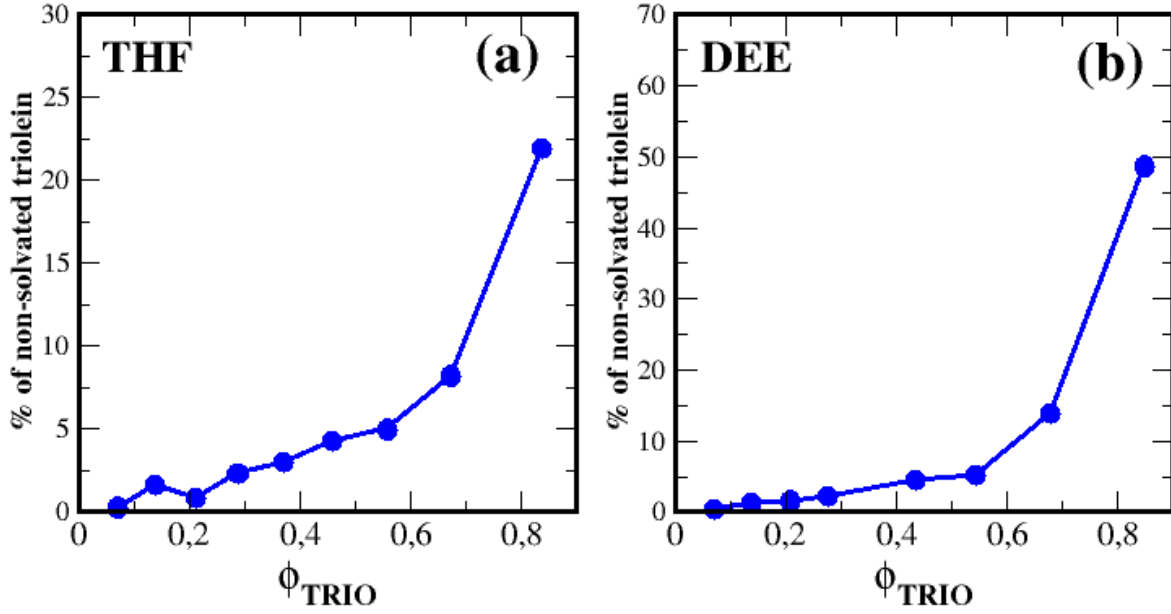


Figure 53: Free triolein as a function of volume fraction of triolein along the phase boundary.

Since methanol-methanol interactions are dominated by hydrogen bonding, radial distribution functions of hydrogen binding sites may shed light on aggregate formation. Therefore, site-to-site radial distribution functions were examined, focusing on the hydrogen bonding between methanol-methanol at different volume fractions of triolein in the ternary mixtures. Results are depicted in Figure 54. We observe a significant increase in peak heights of O_M-H_M RDFs as the volume fraction of triolein increases, implying a higher likelihood of aggregation with increase in triolein [280]. This corresponds to binary interactions in which the χ_{23} is strongly preferred over χ_{12} and χ_{13} . The RDFs for the same systems as functions of simulation time are presented in Figure 55. In the system where complete miscibility is predicted, the peak height and positions do not change Figure 55(a) as the simulation progresses. As shown in Figure 55(b), an increase in the intensity of g_{AB} peaks, is observed as the simulation progresses in the system with a high triolein volume fraction in which aggregation is predicted.

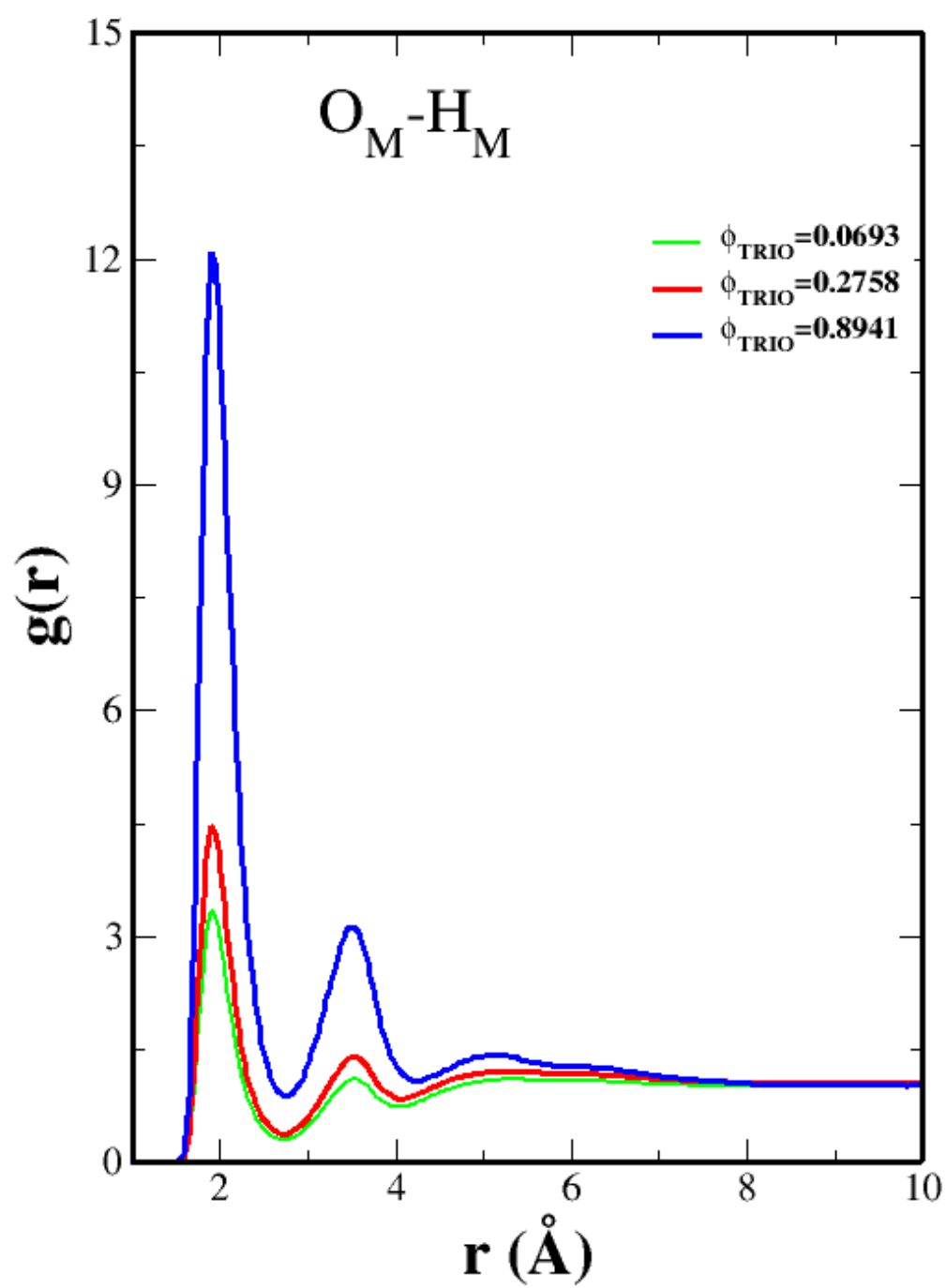


Figure 54: RDFs of MeOH-MeOH for OM-HM at different volume fractions of triolein.

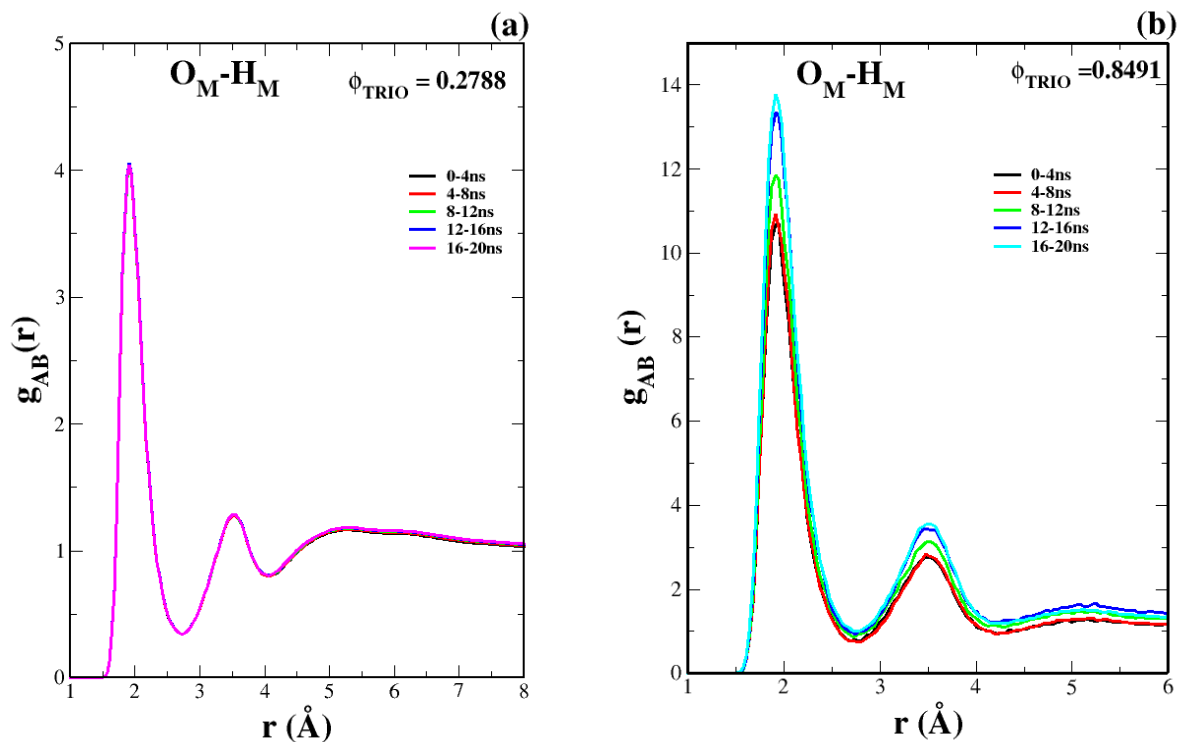


Figure 55: RDF for methanol-methanol O-H interactions in systems where miscibility is observed (a) and where aggregation is observed (b). The data presented here is for triolein/methanol/DEE ternary mixtures.

The effect of temperature on the binary interaction parameters was also investigated and results are shown in Figure 56(a & b). As expected, an increase in temperature is causing an improvement in the binary interactions between methanol and triolein as shown by a decrease in the χ_{12} values in the entire range studied[247,252]. However, this behavior was not observed in the triolein/THF and methanol/THF binary interactions i.e., χ_{13} and χ_{23} where temperature increase weakened the interactions[260]. This suggests that an increase in temperature promotes self-association of the pure components rather than the cross-interactions which results in dispersive forces dominating [281]. However, these repulsions are having a positive effect on the triolein/methanol interactions. It must be noted that the interactions between triolein/THF and THF/methanol (χ_{13} and χ_{23}) are still stronger than the χ_{12} . Similar behavior is noted for triolein/DEE/methanol (Figure 56(b)).

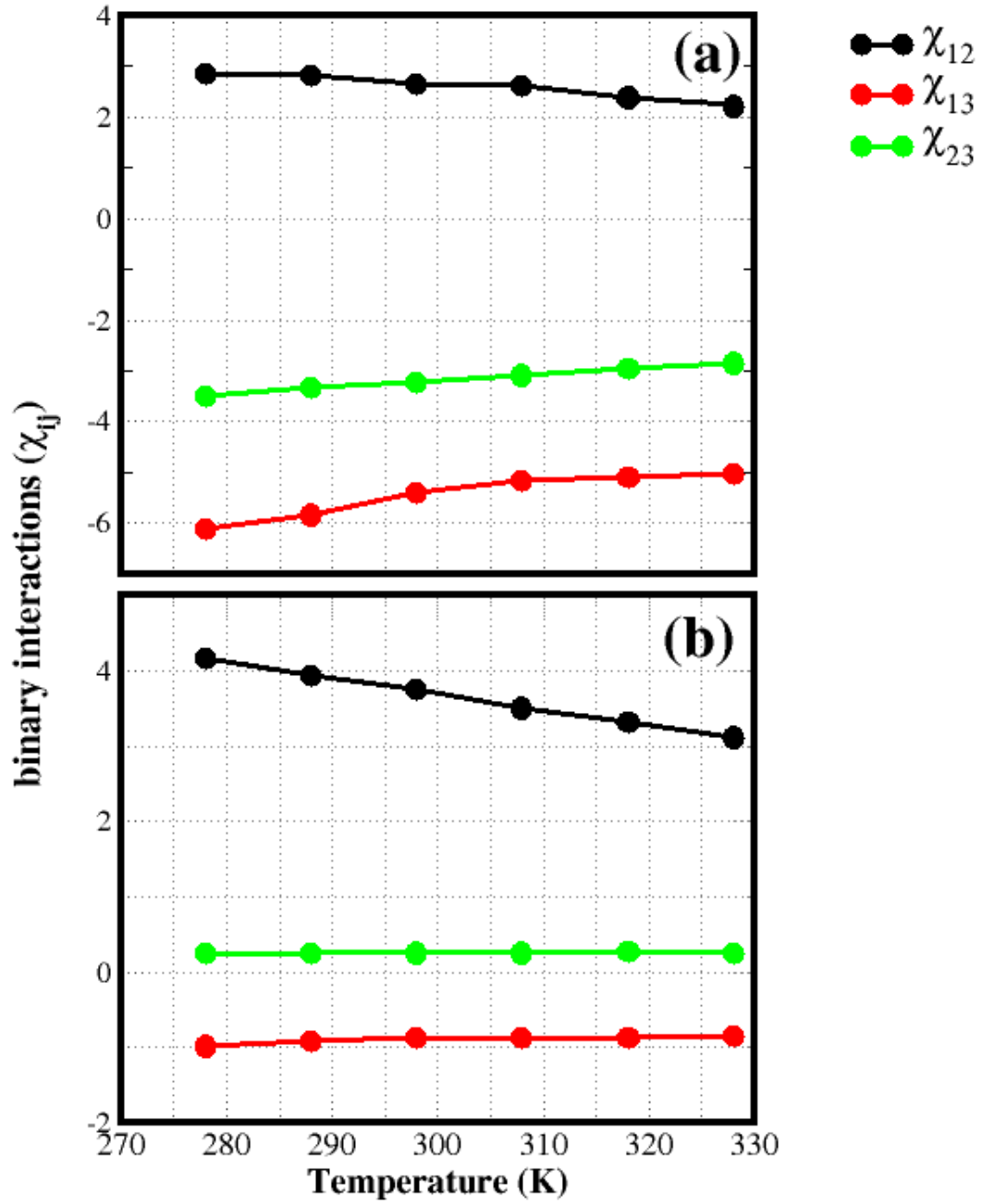


Figure 56: Calculated binary interaction parameters at different temperatures (a) triolein/methanol/THF ternary mixture with composition of $\phi_{TRIO} \approx 0.45$, $\phi_{THF} = 0.243$ and $\phi_{METH} = 0.299$ and triolein/methanol/DEE ternary mixture with composition of $\phi_{TRIO} \approx 0.137$, $\phi_{DEE} = 0.569$ and $\phi_{METH} = 0.294$.

5.3.3 Change in the free energy of mixing

Free energies of mixing ΔG^m were calculated along the experimental phase boundary for the ternary mixtures containing THF as one of the components and results are shown in (Figure 57(a) and Table 5. 2). With the exception of the point at ϕ_{TRIO} of 0.837, the values of ΔG^m obtained are all slightly negative. The enthalpic gain ΔH_m and the entropic loss ΔS_m (Figure 58) are almost cancelling each other showing that the system is closer to equilibrium at the compositions and that the system is in phase boundary where there is coexistence of mixed and unmixed components[247,282]. The high values of ΔG^m and ΔH_m are observed at very high triolein composition i.e., of ϕ_{TRIO} of 0.837, showing that there is phase separation at those compositions[249]. The high values of ΔG^m corresponds to the high values of interaction parameters are also obtained as discussed in the previous section. The expected values of ΔG^m along the phase boundary should be zero or closer to zero because of the metastability of the mixture[283]. From our results, all the data points do not meet this criterion. However, because the simulation involved only one triglyceride type, this is not unexpected. Moorthy et al. observed that the thermodynamic properties of triglycerides depend on their structure and saturation[284]. Therefore, the triolein/methanol/cosolvent is probably insufficient to accurately reproduce the thermodynamic properties of oil/methanol/cosolvent. With the exception of very high triolein compositions, the model predicts spontaneous mixing of the three components. Deviation is observed in mixtures with high ϕ_{TRIO} , which can be attributed to large differences in the molecular volumes of triolein and solvents, resulting in strong self-interaction and weak cross interactions and a high probability of phase separation, resulting in very high values of ΔG^m [227]. This behavior is hardly observed in experiments. In the system containing DEE, (Figure 57 (b) and Table 5. 3) the free energy of mixing is still slightly negative at all compositions except for points with volume fraction of triolein $\phi_{TRIO} > 0.67$. This shows mixing in most compositions. The enthalpy and entropy of mixing were also negative[247]. The phase separation is again observed at higher volume fractions of triolein as shown by largely positive values of free energy of mixing. The snapshot in this region (Figure 47(d)), shows stronger self-association as indicated by formation of aggregates.

The ΔG^m values were also calculated for mixtures with constant triolein volume fractions as described in section 5.3.2 and results are shown in Figure 57(c-d). Figure 57(c) is the plot of ΔG^m against the ϕ_{THF} obtained in the system with fixed ϕ_{TRIO} and Figure 57(d) is for the ternary mixture containing DEE. As expected as one moves from the biphasic to single phase

part of the ternary diagram, the values of ΔG^m also change from positive to negative. This proves that mixing is not spontaneous in the two-phase region while it is spontaneous in single phase as expected. The values of ΔG^m in the mixtures containing DEE are less negative than those containing THF showing slightly weaker interactions. As discussed earlier, the mixing is largely driven by the dispersal of both methanol and triolein in cosolvent.

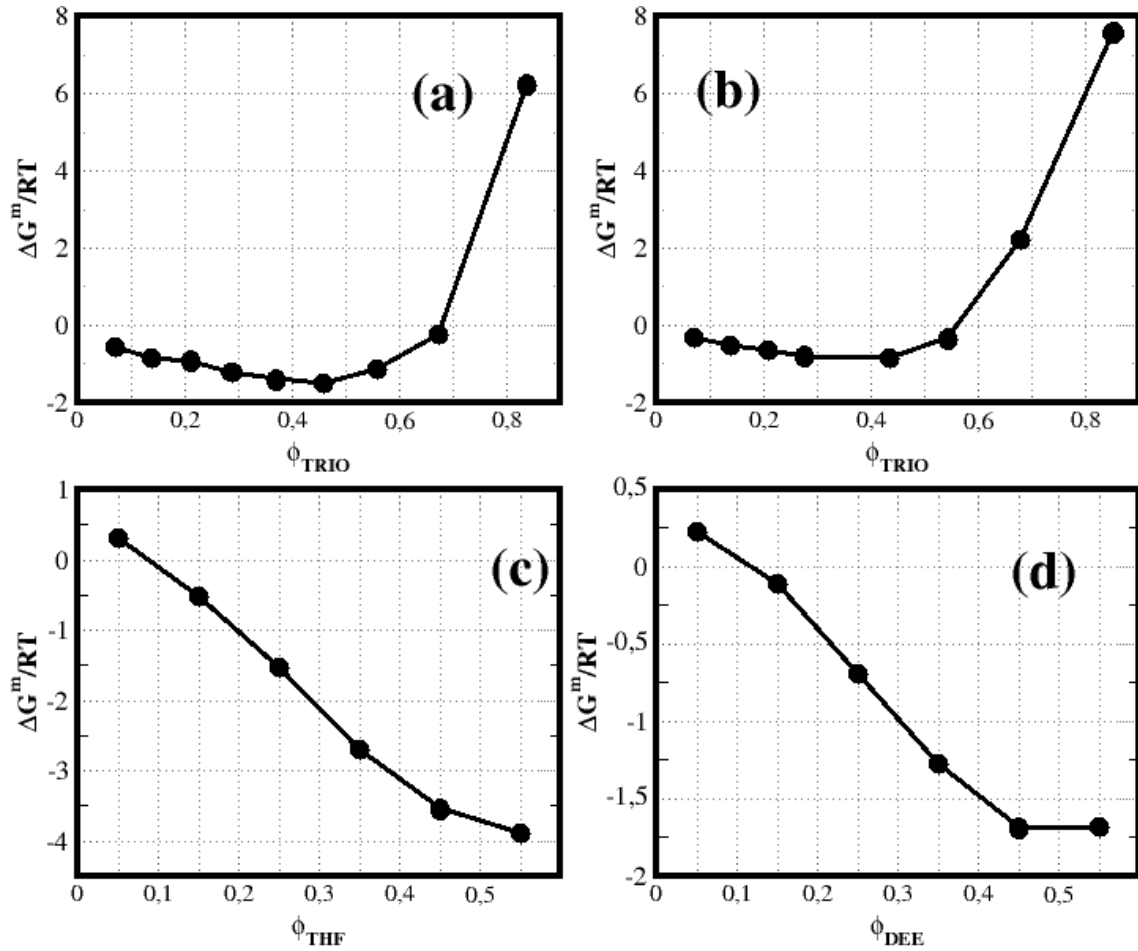


Figure 57: The change in the Gibbs free energy along the experimental phase boundaries, (a) THF/methanol/triolein, (b) DEE/methanol/triolein. (c) and (d) are changes in the Gibbs free energy calculated at fixed triolein composition ($\phi_{TRIO} = 0.4$) for mixtures THF/methanol/triolein and DEE/methanol/triolein respectively. Experimental data for the phase boundaries are from reference [201].

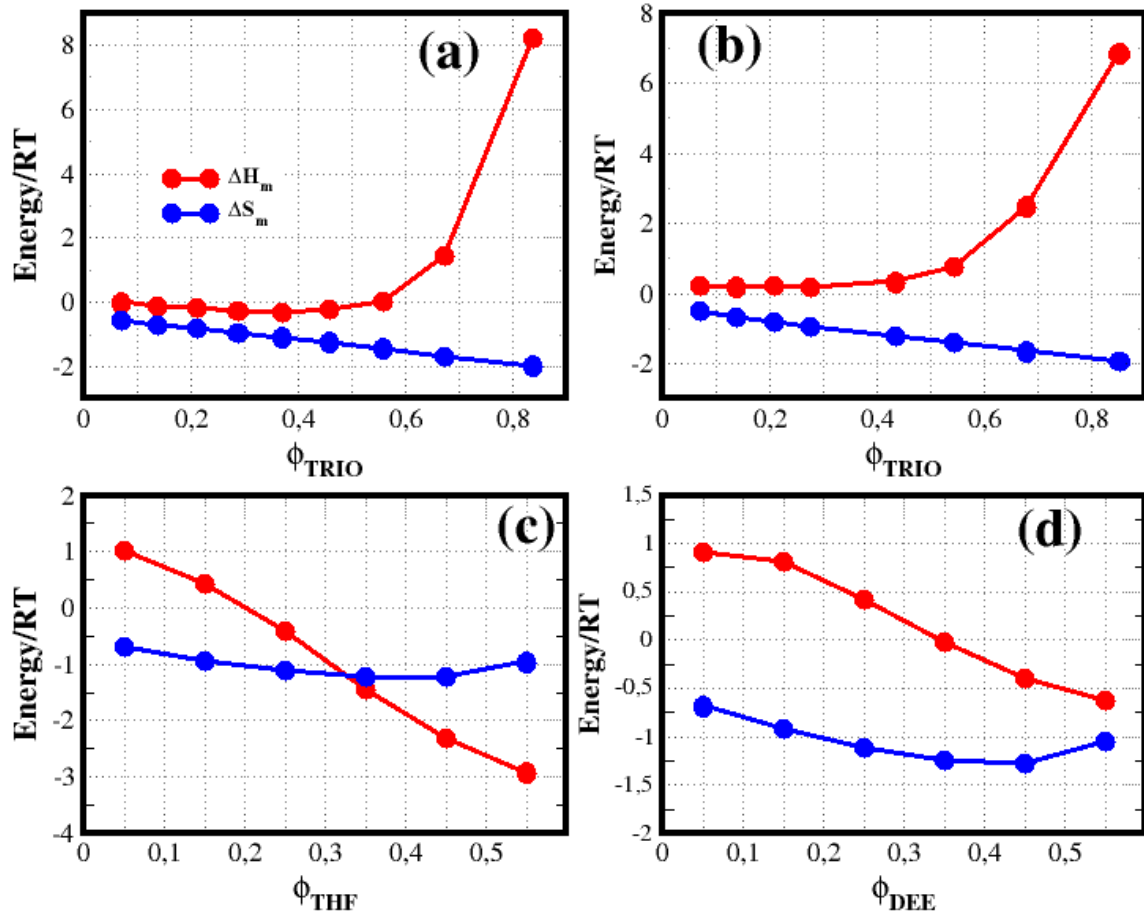


Figure 58: Change in the enthalpy, ΔH_m and entropy, ΔS_m , of mixing along the experimental phase boundaries, (a) THF/methanol/triolein, (b) DEE/methanol/triolein. (c) and (d) are changes in the enthalpy and entropy of mixing calculated at fixed triolein composition ($\phi_{TRIO} = 0.4$) for mixtures the mixtures THF/methanol/triolein and DEE/methanol/triolein respectively.

Equations 5.1 and 5.11 show that the free energy of mixing has both enthalpic contributions and entropic contributions and that only the enthalpic contribution is temperature dependent. With this in mind, we calculated the free energy of mixing as a function of temperature and results are presented in Figure 59(a & b). The expectation is that increase in temperature should lower ΔG^m . The two systems are showing contradicting behavior. With THF as a cosolvent (Figure 59(a), ΔG^m initially increases with temperature up to 318K and decreases thereafter. However, it should be noted that ΔG^m are not changing that much. The increase in temperature has minimal effect in this system[260]. With DEE as a cosolvent (Figure 59(b)), increasing the temperature results in increase in spontaneity as shown by more negative

values of ΔG^m . Just like in the system with THF as a cosolvent, the increase in temperature has little effect in the change in the free energy of mixing in this system.

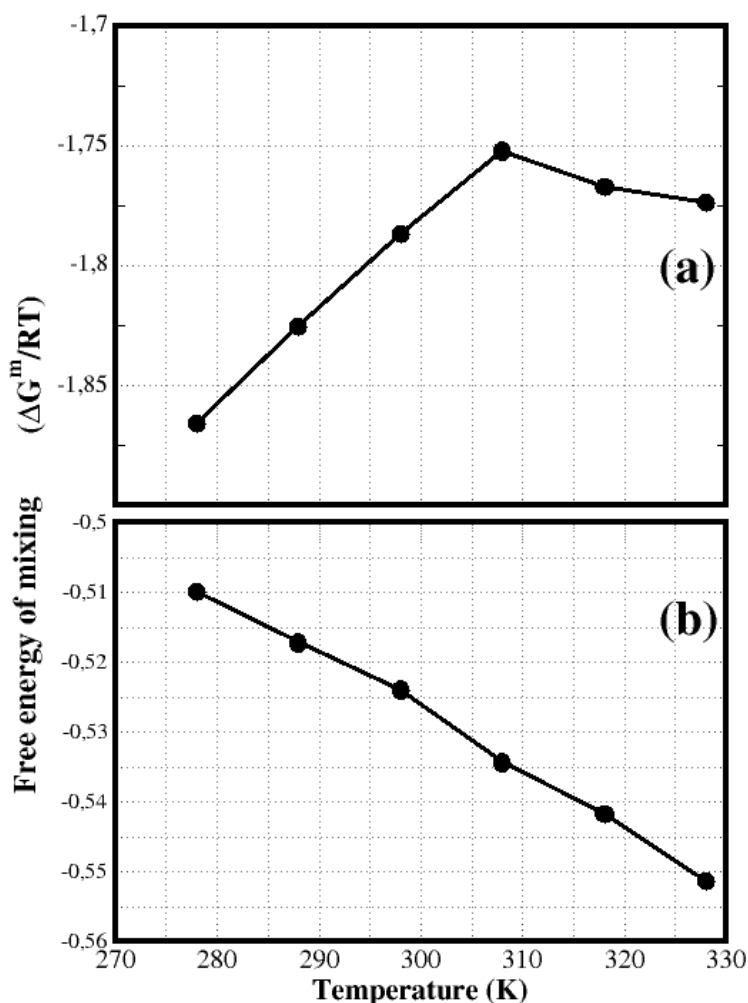


Figure 59: Calculated Gibbs free energy of mixing (ΔG^m) of mixing as a function of temperature, (a) THF/methanol/triolein, (b) DEE/methanol/triolein mixtures.

5.3.4 Change in the chemical potentials and activity coefficients

Changes in the chemical potentials of the components of the ternary mixtures along experimental phase boundaries plotted against the volume fractions of triolein are shown in Figure 60(a & b). These plots should be “U” shaped in accordance with equations (5.16), assuming that the simulated mixtures are also at the phase boundary. $\Delta\mu_{TRIO}$ and $\Delta\mu_{COSOLVENT}$ plots are nearly “U” shaped as expected, while $\Delta\mu_{METH}$ is less so. The deviations could be due to the inadequacy of the triolein/methanol/cosolvent model but could also be simply due to the fact that the simulated system for the triolein model is quite far from

the phase boundary. The chemical potential $\Delta\mu_i$ is indicative of the availability of component i , to interact with other components. Negative $\Delta\mu_i$ values show that attractive interactions between component i , and the other components are favorable compared to self-interaction[285,286]. In both cosolvents mixtures, the values of $\Delta\mu_{METH}$ are only slightly negative due to methanol's strong propensity to self-associate. For the triolein/methanol/THF ternary system, the highest values of the chemical potentials correspond to the $\phi_{TRIO} > 0.8$ (Table 5. 2). For the triolein/methanol/DEE ternary system, (Figure 60(b)), the highest values are observed at triolein compositions i.e., $\phi_{TRIO} < 0.60$ where $\Delta\mu_{TRIO}$ values are positive showing dominance of repulsive forces in that region. In the same region, $\Delta\mu_{METH}$ and $\Delta\mu_{THF/DEE}$ are also positive, which is indicative of dominance of self-association. The ΔG^m values in that region are also very highly positive (Figure 57(a & b)). In the region $0.07 < \phi_{TRIO} < 0.7$ the values of $\Delta\mu_{TRIO}$ are negative showing dominance of attractive forces between triolein and other components. For the ternary mixture containing DEE/methanol/triolein (Figure 60(b), the change in chemical potential ($\Delta\mu_{TRIO}$) is negative at all compositions except $\phi_{TRIO} > 0.6$. This indicates stronger attractive forces between triolein and other two components, hence favorable interactions.

Figure 60(c-d) show the variation of $\Delta\mu_i$ for mixtures in which triolein is fixed at $\phi_{TRIO} = 0.40$, with the cosolvents THF and DEE respectively. The chemical potential of triolein, $\Delta\mu_{TRIO}$ becomes less positive as $\phi_{COSOLVENTS}$ increases, showing improvements in the interactions. In both ternary systems, $\Delta\mu_{TRIO}$ changes from positive to negative indicating more favorable interactions between triolein with cosolvents and methanol as $\phi_{COSOLVENT}$ increases. The chemical potentials of cosolvent($\Delta\mu_{Cosol}$) is relatively constant at all cosolvent compositions with the exception to a point at $\phi_{COSOLVENT} = 0.07$ showing that it is in equilibrium with both triolein and methanol [286]

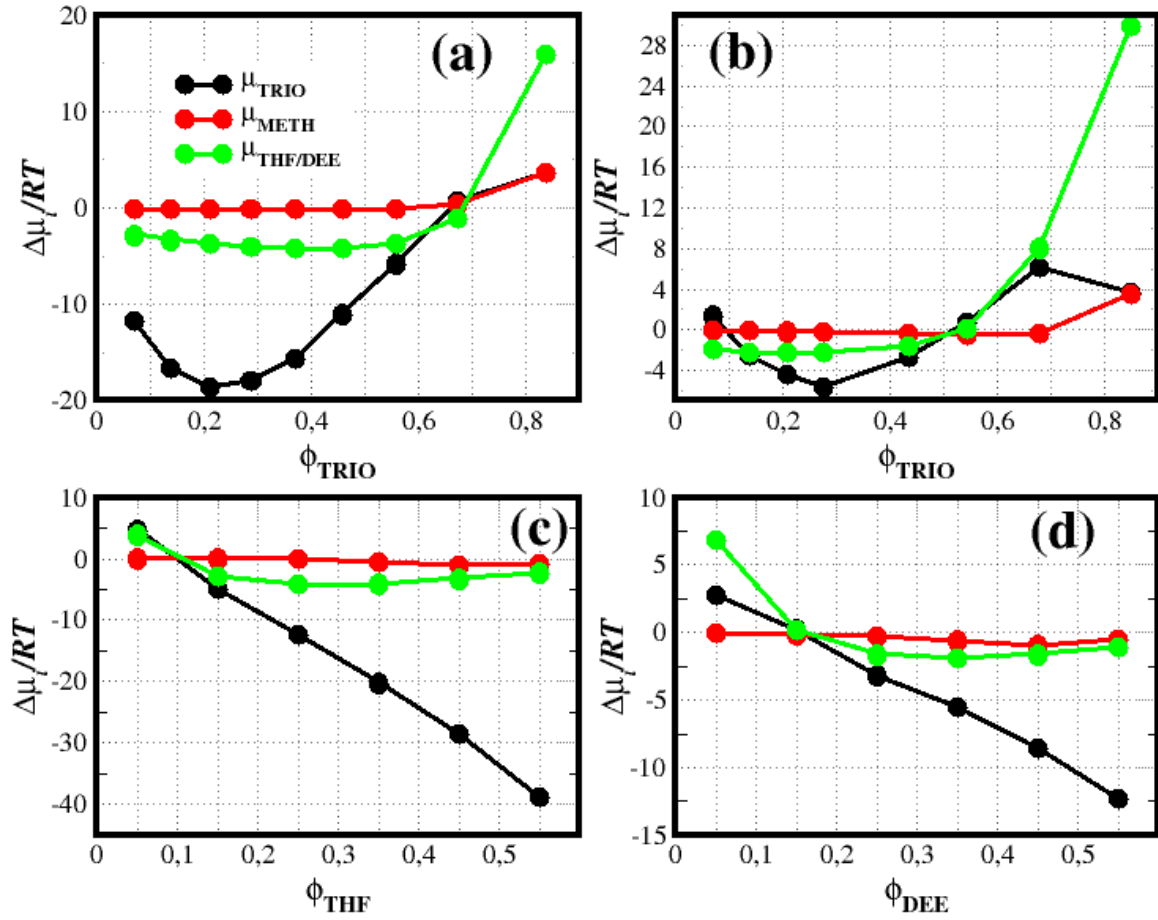


Figure 60: Calculated chemical potentials ($\Delta\mu_i$) along the experimental phase boundaries, (a) THF/methanol/triolein (b) DEE/methanol/triolein. (c) and (d) chemical potentials were calculated at fixed triolein composition ($\phi_{TRIO} = 0.4$) for mixtures THF/methanol/triolein and DEE/methanol/triolein respectively. Experimental data for the phase boundaries are from reference [201].

The effect of temperature on the chemical potential was also investigated. Presented in Figure 61 is the plot of $\Delta\mu_i$ as a function of temperature. All values of the chemical potentials are negative in the range studied showing an increase in the attractive forces as temperature increases. Among the components, the chemical potential of triolein is the one that is mainly affected by this increase as shown by the values becoming more negative. This behavior is mainly observed in the system with DEE as cosolvent (Figure 61(b)). The values of μ_{METH} are very close to zero which is indicative of its propensity to self-associate.

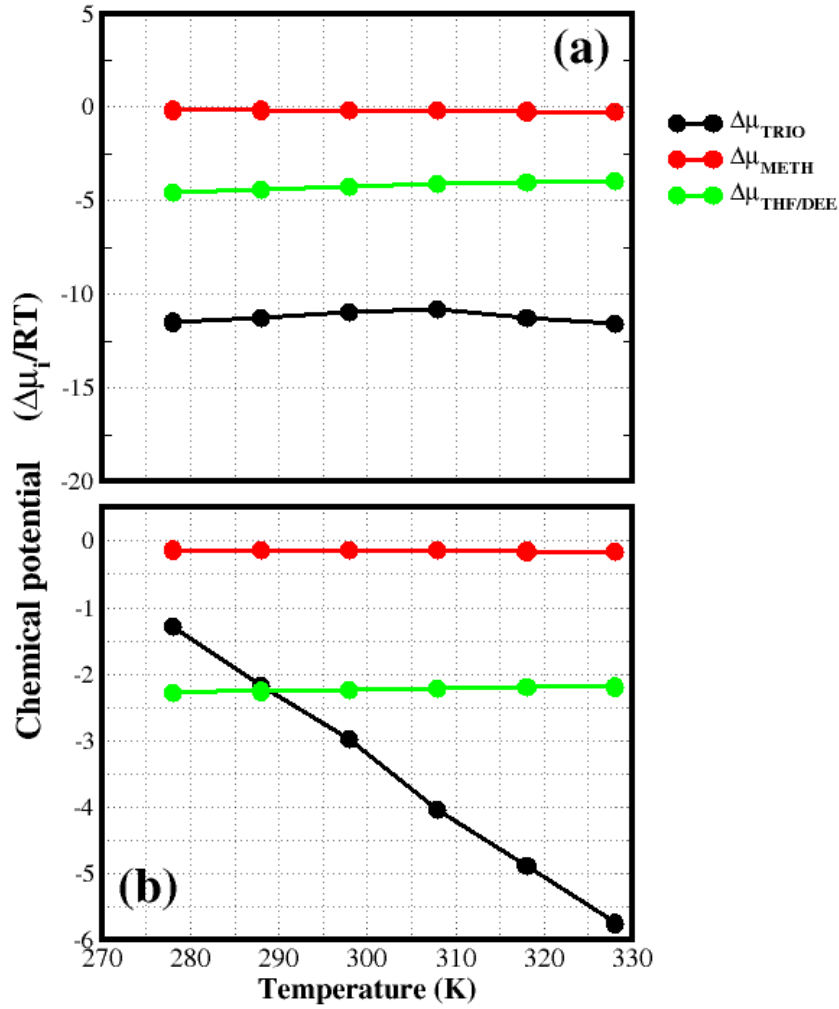


Figure 61: Calculated chemical potentials, $\Delta\mu_i$, as a function of temperatures (a) triolein/methanol/THF ternary mixture with composition of $\phi_{TRIO} \approx 0.45$, $\phi_{THF} = 0.243$ and $\phi_{METH} = 0.299$ and (b) triolein/methanol/DEE ternary mixture with composition of $\phi_{TRIO} \approx 0.137$, $\phi_{DEE} = 0.569$ and $\phi_{METH} = 0.294$.

The activity of a component (a_i) in a mixture is one way of comparing the strength of its self-interaction in comparison to its interactions with other components. Usually, if $a_i < 1$, it is an indication that component i interacts strongly with other components hence a single phase is predicted, otherwise stronger self-interactions are observed compared to cross-interactions and in this case a phase separation is predicted. With this in mind, the activities of the components of the mixtures were derived from chemical potentials calculated from Flory-Huggins's theory using equation 5.18 and compared to those calculated via the UNIFAC (Universal Functional Activity Coefficient) contribution method model.

$$a_i = e^{\mu_i} \quad (5.18)$$

The UNIFAC Method is group contribution method that is used to predict the activity coefficient γ_i of a component in a mixture. The activity coefficient is the sum of the combinatorial γ_i^C and the residual terms γ_i^R and is calculated using equation (5.19).

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (5.19)$$

The combinatorial term is calculated using equation (5.20) and accounts for both the size and shapes of the molecules. In equation 5.20, z is the coordination number, φ_i is the volume fraction, θ_i is the surface area fraction, x_i is the mole fraction of component i .

$$\ln \gamma_i^C = \ln \frac{\varphi_i}{x_i} + 1 - \frac{\varphi_i}{x_i} - \frac{z}{2} q_i \left(1 + \ln \left(\frac{\varphi_i}{\theta_i} \right) - \left(\frac{\varphi_i}{\theta_i} \right) \right) \quad (5.20)$$

The residual term accounts for the interaction between the groups in the mixture. It is calculated using the equation (5.21), where $\ln \Gamma_k$ is the activity coefficient for each group k and the activity coefficient of an isolated group in a solution containing just molecules of type i is given by $\ln \Gamma_k^{(i)}$.

$$\ln \gamma_i^R = \sum_k v_k^{(i)} \left[\ln \Gamma_k - \ln \Gamma_k^{(i)} \right] \quad (5.21)$$

The UNIFAC activities were then calculated according to equations 5.21 as implemented in Thermos software [287] while the activities from chemical potentials were calculated using equation 5.18. The results are displayed in Figure 62, as well as in Table 5. 6 and Table 5. 7. The activities calculated for a ternary system of triolein/methanol/THF along phase boundaries are depicted in Figure 62(a) (NB: values calculated using Flory-Huggins at high volume fractions of triolein i.e., $\phi_{TRIO} > 0.67$, are not shown in the figure). At lower of volume fraction of triolein ϕ_{TRIO} i.e., $0.07 < \phi_{TRIO} < 0.67$ there is a good agreement between the activities derived from our chemical potential and those derived from UNIFAC model. All calculated activities were below 1 predicting a single-phase system. However, at higher ϕ_{TRIO} i.e., > 0.67 there is a deviation where UNIFAC shows values greater than 1 only for the methanol component while Flory Huggins predicts phase separation which agrees with our calculated ΔG^m . The snapshots of these regions are clearly predicting phase separation (Figure 47(c-d)).

For the ternary system containing DEE (Figure 62(b)), at low ϕ_{TRIO} both Flory-Huggins and UNIFAC calculated activities are greater than one predicting phase separation. ΔG^m at this volume fraction is very close to zero showing the presence of mixed and unmixed components. For $0.1 < \phi_{TRIO} < 0.54$ both UNIFAC and Flory-Huggins models predict a single phase. The activities for $\phi_{TRIO} > 0.67$ (not shown in the plot) are positive and very high. Phase separation is observed when at least one component in the mixture has an activity greater than 1.

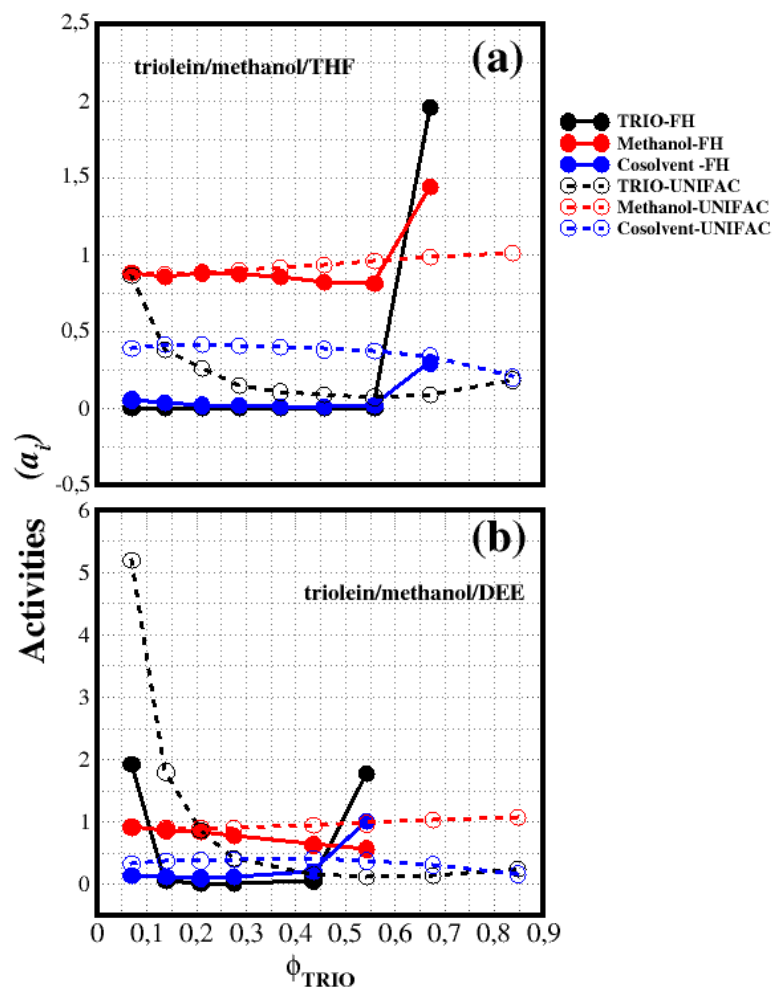


Figure 62: Calculated activities along the experimental phase boundaries of reference [13]. (a) System containing THF and (b) is system containing DEE. Solid lines (Flory- Huggins calculated activities and broken lines (UNIFAC calculated activities).

Table 5. 6: UNIFAC and Flory-Huggins activities calculated along the experimental phase boundaries, for the ternary mixture of THF/methanol/triolein.

	Flory Huggins Calculated			UNIFAC calculated.		
ϕ_{TRIO}	a_{TRIO}	a_{METH}	a_{THF}	a_{TRIO}	a_{METH}	a_{THF}
0.069	8.1E-06	0.881871	0.05757	0.863417	0.881653	0.390541
0.137	6.05E-08	0.853786	0.035286	0.382915	0.872882	0.41855
0.212	8.24E-09	0.883926	0.023983	0.25998	0.881267	0.412203
0.286	1.59E-08	0.873556	0.017735	0.145813	0.894682	0.409465
0.370	1.63E-07	0.856569	0.014066	0.109641	0.912262	0.398786
0.458	1.65E-05	0.818202	0.014228	0.087388	0.934635	0.385969
0.558	0.002996	0.808169	0.022616	0.075482	0.959523	0.372756
0.672	1.951894	1.435823	0.300124	0.08692	0.98133	0.341384
0.837	34.49899	35.27378	7202941	0.187291	1.010306	0.205554

Table 5. 7: UNIFAC and Flory-Huggins activities calculated along the experimental phase boundaries, for the ternary mixture of DEE/methanol/triolein[201].

	Flory Huggins Calculated			UNIFAC calculated.		
ϕ_{TRIO}	a_{TRIO}	a_{METH}	a_{DEE}	a_{TRIO}	a_{METH}	a_{DEE}
0.069	1.919721	0.917919	0.138461	5.181437	0.90396	0.326985
0.138	0.050721	0.864924	0.106639	1.800877	0.890471	0.371559
0.208	0.011437	0.833175	0.102045	0.849286	0.895389	0.379442
0.276	0.002961	0.773538	0.105941	0.414625	0.900031	0.395528
0.435	0.056444	0.632598	0.201151	0.143803	0.932272	0.406106
0.543	1.771807	0.566658	1.011061	0.116254	0.974071	0.376828
0.677	455.3198	0.612626	2849.788	0.12523	1.031692	0.312425
0.849	38.20628	31.37464	9.11E+12	0.232823	1.065106	0.162535

5.4 Conclusions

The Flory-Huggins theory of solutions has been used to study the thermodynamics of mixing in a ternary system consisting of triolein, methanol and cosolvents (tetrahydrofuran or diethyl ether). Along the phase boundary, the binary interaction parameters between methanol and cosolvent remain relatively constant. The Gibbs free energy of mixing (ΔG^m) in this region shows both positive and negative values, indicating the presence of both mixed and unmixed phases.

Thermodynamic parameters were also calculated for the region with a fixed volume fraction of triolein ($\phi_{TRIO} = 0.40$) which encompasses both single phase and two-phase regions of the ternary mixture. An increase in the volume fraction of cosolvents does not seem to have any major effect on the interactions between triolein and methanol as indicated by χ_{12} interaction parameters. However, triolein/cosolvent and methanol/cosolvent interactions are improved greatly with the addition of cosolvent which leads to the conclusion that mixing is driven by the dispersal of both methanol and triolein in cosolvent. The calculated ΔG^m changed from positive to negative when one moves from two phase to single phase of the ternary diagram, with an increase in the volume fraction of cosolvents as dispersal promotes mixing of the components. The increase in temperature improves the interactions between methanol and triolein but has minimal effect on triolein/cosolvent and methanol/cosolvent interactions.

Comparison of THF and DEE as cosolvents suggests that THF has stronger interactions with both methanol and triolein and may be more effective as a cosolvent based on considerations of the relative amounts needed to form a single phase.

Finally, the activities of components (a_i) calculated from the Flory-Huggins derived chemical potentials were compared to those derived using the UNIFAC model. In the region where UNIFAC predicts phase separation i.e., $a_i > 1$ our Flory-Huggins derived activities are also greater than 1. There is a good agreement between activities calculated by the UNIFAC and Flory Huggins models. However, there were minor differences observed at higher triolein compositions. In summary, we conclude that the simple Flory-Huggins model can be applied to study oil/methanol/cosolvent mixtures using molecular dynamics derived parameters.

CHAPTER 6

Decarboxylation of methyl palmitate on binary nickel molybdenum catalysts

6.1 Introduction

In Chapters 4 and 5 the role of cosolvents in improving miscibility of oil and methanol during transesterification was investigated. Interactions that occur between methanol, cosolvent and triglyceride and the thermodynamic properties of such mixtures were studied. Chapter 6 focuses on the final product, biodiesel, with the aim of improving the flow properties and oxidative stability by converting it to green diesel.

There are three ways in which biodiesel can be converted to hydrocarbons (green diesel), namely hydrodeoxygenation (HDO), decarboxylation, and decarbonylation. The difference between the three processes was explained in CHAPTER 2, section 2.2.2. The advantage of decarboxylation is that unlike HDO and decarbonylation, water, which has a tendency to deactivate catalysts is not produced[125]. Catalysts like Rh/ZrO₂[151], nickel metal catalysts supported on (SiO₂, Al₂O₃, and HZSM-5)[288], Ru supported on HZSM-5 zeolites[126] and even unmodified HZSM-5 zeolites[289] have been used to upgrade FAMEs to hydrocarbons.

Numerous studies have demonstrated the potential of Ni-based catalysts for low-temperature deoxygenation reactions[290–292]. Its inexpensive cost and excellent electrical qualities make nickel-based catalysts very popular. However, Ni on its own has low activity[293]. To improve its limitations, metal promoters and supports are sometimes used. Studies have shown that the catalytic activity for the deoxygenation reactions can be enhanced by the addition of high valence transition metal elements like molybdenum to Ni-based catalysts resulting in the formation of bimetallic catalysts or alloys[294]. These catalysts have been found to have higher catalytic activity than monometallic catalysts[291]. The synergetic interaction between the two metals results in physical promotion provided by one of the metals. Studies have demonstrated that Ni and Mo interact synergistically, increasing both the charge density on the surface of Ni atoms and the concentration of oxygen vacancies in the catalyst which increases the activity and

selectivity of conversion to alkanes[134]. When it comes to conversion of FAMES to green diesel, sulphided NiMo or CoMo catalysts are most frequently used[128,149]. However, these sulphided catalysts have been found to contaminate products through sulfur-leaching[128]. This has forced researchers to move away from the sulphided catalysts. Senol et al.[128,149] investigated the HDO of methyl heptanoate using NiMo/ γ -Al₂O₃ and CoMo/ γ -Al₂O₃ catalysts. The study found that NiMo/ γ -Al₂O₃ catalyst showed higher selectivity of heptane as compared to CoMo/ γ -Al₂O₃ catalyst. This was due to a better synergistic interaction between Ni and Mo in the former compared to Co and Mo. Therefore, it can be concluded that a bimetallic catalyst containing both Ni and Mo will have the ability to convert FAMES to hydrocarbons through decarboxylation.

In a study conducted by Kumar et al.[295], a bimetallic nickel/molybdenum catalyst was examined for stearic acid HDO. The Raman spectrum characterization demonstrated the presence of nickel molybdate (Raman bands at 709 and 964 cm⁻¹) in calcined catalysts and NiMo in all reduced catalysts. The NiMo alloy and NiMoO₄ exhibited higher catalytic activity in comparison to the Ni catalyst because of the synergy that existed between Ni and Mo. Nickel molybdate (NiMoO₄) is one of the mixed metal oxides which has received considerable interest from researchers. It has been used as a catalyst for processes like hydrodesulphurization[150], hydrodenitrogenation of petroleum[232], oxidative dehydrogenation of alkanes [296–300] and also as a supercapacitor[301]. It is a chemically stable and non-toxic chemical.

NiMoO₄ exists as three polymorphs and two of which are stable at room temperature. The stable polymorphs are α -NiMoO₄ and β -NiMoO₄ and have monoclinic crystal structure with a space group of C2/m[292]. The difference between the two is in coordination around Molybdenum atoms. In α -NiMoO₄ phase, Mo is stabilized in distorted octahedral coordination while it is in distorted tetrahedral coordination in β -NiMoO₄. The stability of the two phases also differs, the α -NiMoO₄ phase is stable from room temperature to 650°C while the β -NiMoO₄ is stable between 250 to 700°C.

Sancheti et al. [125], synthesized potassium promoted nickel molybdenum catalyst supported in mesoporous titanosilicate (NiMoK /TS-1). This catalyst was then used in the decarboxylation of methyl palmitate (MP) to produce green diesel[125]. The proposed mechanism in the decarboxylation of MP begins with MP being adsorbed on the metal center via methoxy oxygen which increases the oxidation of the metal center from Mⁿ⁺¹ to Mⁿ⁺², followed by the abstraction of β -hydrogen of MP by oxygen in the metal oxide surface resulting in the formation of a double

bond and evolution of carbon dioxide and an olefin. The adsorbed methyl radical and hydrogen radical later desorbs methane gas. The decarboxylation process of methyl palmitate was successful with a selectivity rate of 87% towards $C_{15}H_{30}$. Figure 63 shows the proposed mechanism for the decarboxylation process. However, it is not clear which metal center is the active site for initial adsorption.

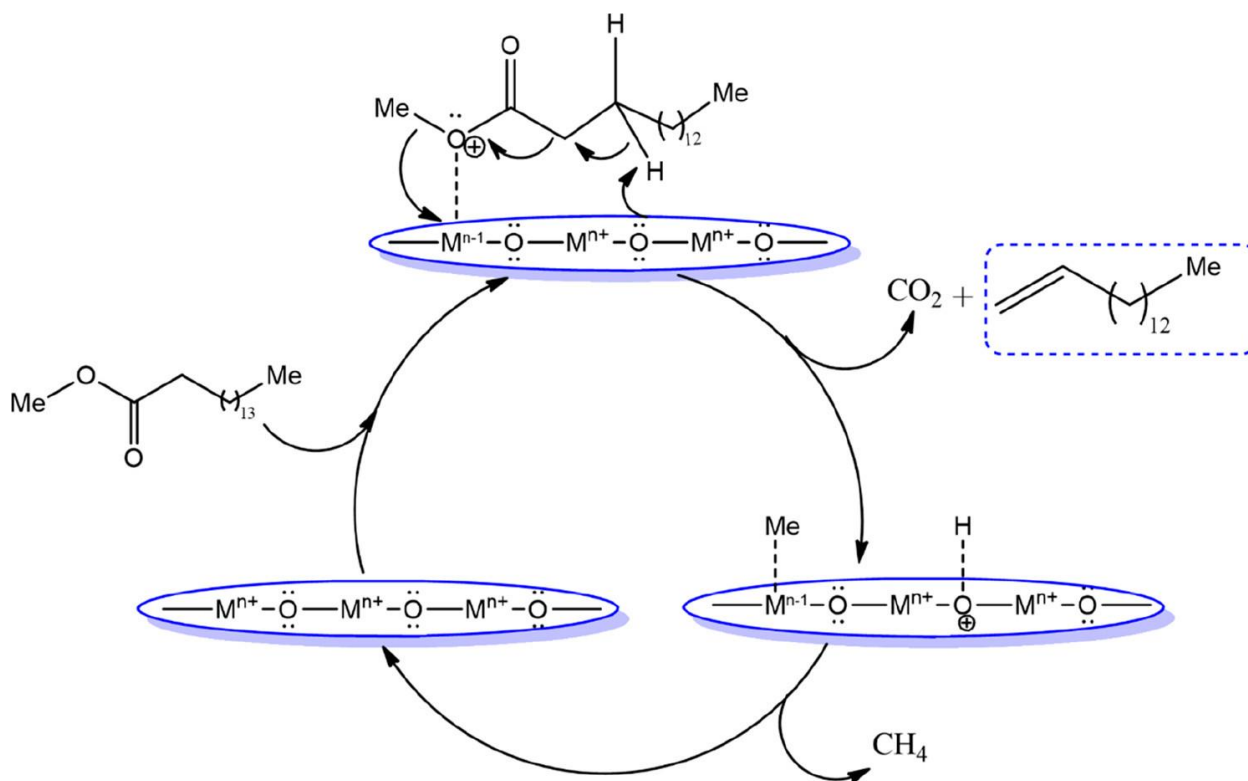


Figure 63: Proposed mechanism for the decarboxylation of methyl Palmitate. Source ref [125]

In this chapter, we will investigate the decarboxylation of MP with the presence of binary NiMo catalysts using the Reactive Force Field (ReaxFF) molecular dynamics. Our main objective is to compare the activity of 110 and 021 planes α -NiMoO₄, β -NiMoO₄ phases, and the alloy Ni₃Mo (101) plane. We have chosen these surfaces based on their strong peaks in XRD[292,302,303].

ReaxFF is a bond order based reactive force field that was introduced by van Duin *et al.* [181] in 2001 to bridge a gap between quantum mechanics and experiment[188]. All the parameters used in ReaxFF have been trained with several sets of quantum mechanics data and have been found to be able to reproduce experimental findings. ReaxFF can simulate breakage and formation of

bonds, making it possible to study large-scale reactions at high temperatures and pressures that are usually used experimentally, which is computationally expensive with quantum mechanics-based simulations. ReaxFF has been able to accurately model reactions of hydrocarbons in the presence of catalyst [183], pyrolysis of triolein [138], oxidation of methyl linoleate[304] and oxidation of lignin [305]. These investigations have demonstrated that ReaxFF-based simulations can aid in explaining the reaction mechanisms and kinetics of organic compound interactions with catalysts.

6.2 Computational methods

6.2.1 Preparation of initial configurations

Molecular dynamics with ReaxFF was used to study the decarboxylation of methyl palmitate over nickel molybdate catalyst and nickel molybdenum alloy. This study utilized two polymorphs of NiMoO_4 , namely α - NiMoO_4 and β - NiMoO_4 , shown in Figure 64(a) and Figure 64(b) respectively. These belong to $C2/m$ space group. The crystal structure parameters of α - NiMoO_4 were obtained from the Material Project Crystal database [306,307], with lattice parameters $a = 9.55 \text{ \AA}$, $b = 8.74 \text{ \AA}$, $c = 6.97 \text{ \AA}$, $\alpha = 90.0^\circ$, $\beta = 114^\circ$, and $\gamma = 90.0^\circ$. β - NiMoO_4 crystal vectors were obtained from the Springer Materials database [308], with crystal vectors of $a = 10.13 \text{ \AA}$, $b = 9.28 \text{ \AA}$, $c = 7.02 \text{ \AA}$ and angles $\alpha = 90.0^\circ$, $\beta = 107.2^\circ$, $\gamma = 90.0^\circ$ [308]. Ni_3Mo belongs to the space group $Pmmn$, with crystal lattice parameters being $a = 5.064 \text{ \AA}$, $b = 4.228 \text{ \AA}$, $c = 4.448 \text{ \AA}$ [309,310], (Figure 64(c)). The crystal structure was obtained from the Materials Cloud database[311].

The simulations were conducted on different surfaces, defined by the exposed crystal planes of miller indices (hkl), of 021 and 110 for α - NiMoO_4 and β - NiMoO_4 catalysts (Figure 65), and 101 for Ni_3Mo . METADISE code [312] was used to create the surfaces with the lowest energy and dipole moment. The supercells for simulation were then constructed by duplicating the unit cells 6 times in the a and b direction and 4 times in the c direction using AtomsK software [313].

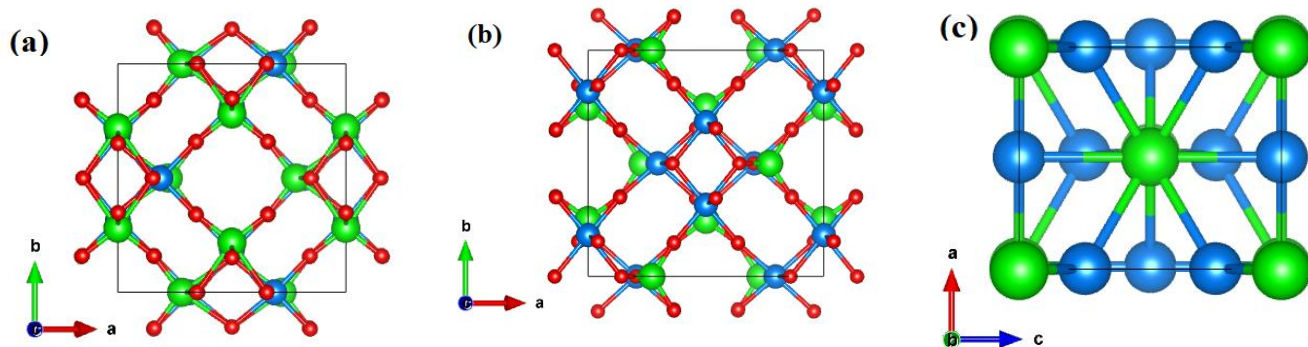


Figure 64: Structures of the unit crystals of (a) α -NiMoO₄ (b) β -NiMoO₄ and (c) Ni₃Mo: Key red-oxygen, blue-Nickel, green- Molybdenum.

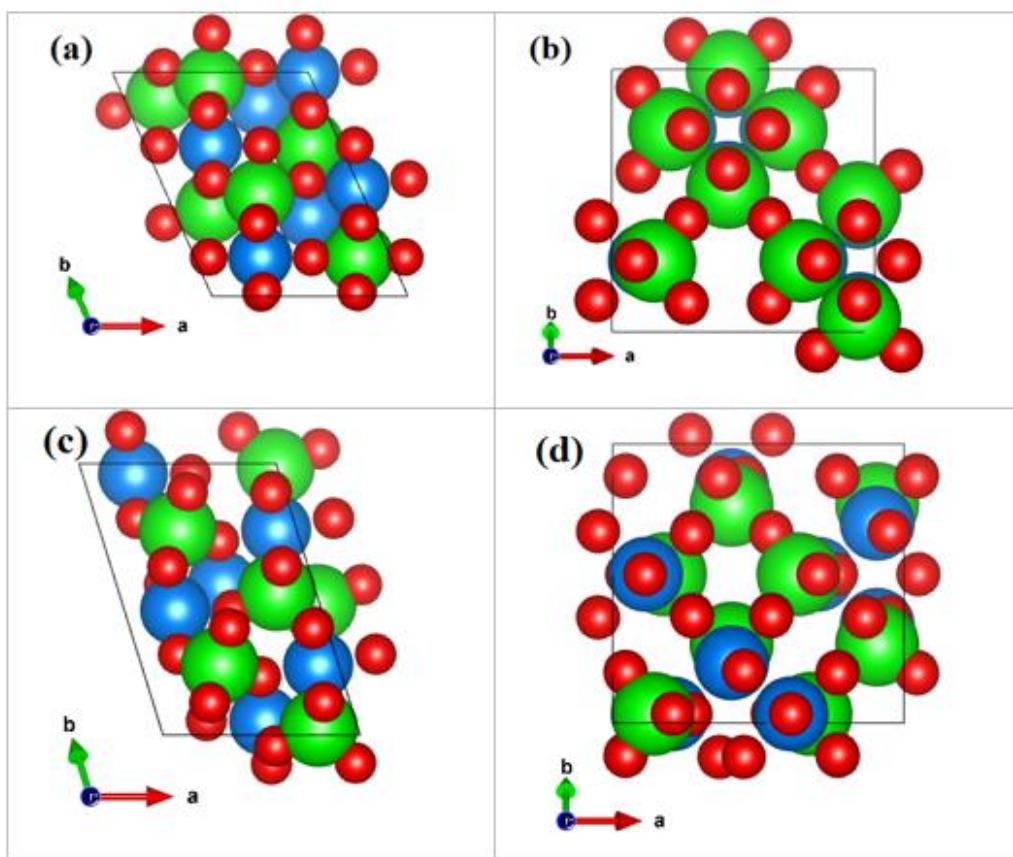


Figure 65: The top view of the surfaces exposed to reactants for NiMoO₄ catalysts. (a) α -NiMoO₄ (110), (b) α -NiMoO₄ (021), (c) β -NiMoO₄ (110), (d) β -NiMoO₄ (021). Key red-oxygen, blue-Nickel, green- Molybdenum.

A vacuum of 40 Å was added to both ends of the supercell along the z-axis. Then, 20 methyl palmitate molecules (Figure 66) were added to the slab using PACKMOL software, with ten on each side. The initial configuration obtained is shown in Figure 67.

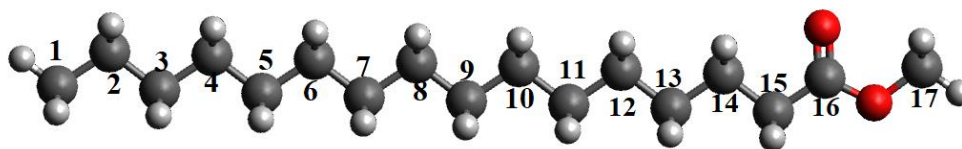


Figure 66: The structure of methyl palmitate molecule showing numbering of carbon atoms.

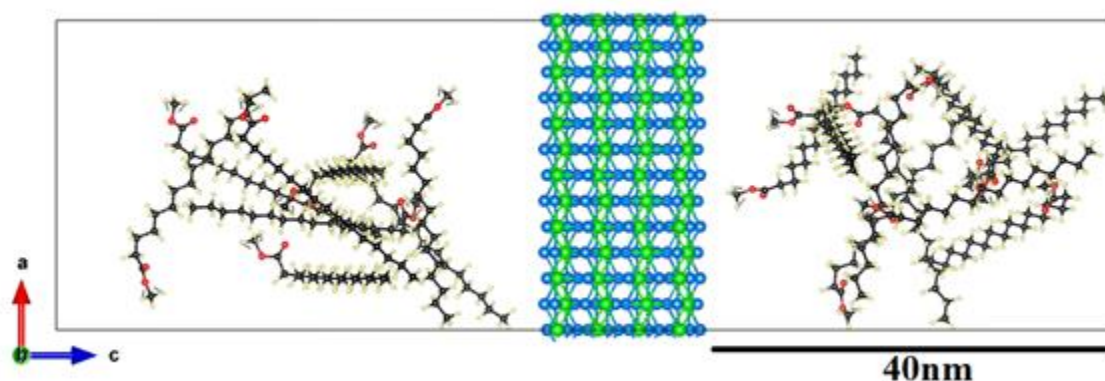


Figure 67: Initial configuration of system generated using AtomsK software[313] for slab duplication and PACKMOL software[314] for molecule insertion

6.2.2 Simulation protocols

To the prepared initial configurations, energy minimisation was performed using the steepest descent algorithm. Presented in Figure 68 is the change in potential energy during the minimisation stage. This was then followed by thermal equilibrations in which the temperature of the system was increased by intervals of 50K until 650K. Equilibration runs were 10ps long and its purpose was to prevent unreasonable initial structures and excessive fragmentation [184]. After equilibration, the dual temperature simulation was used in which the temperature of the catalyst slab was kept constant at 650K while in the region containing FAMEs, the temperature was varied. This made it easy to observe the reactions without melting the catalyst slab [179,183]. The production calculations were carried out under a constant number of particles, volume, and temperature (NVT-MD ensemble) for 100ps. The simulation used a time step of

0.1fs and the temperature was regulated using the Nöse-Hoover thermostat with a damping constant of 100fs. Calculations were carried out using Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) code [199] and Amsterdam modelling suite (AMS)[200]. The ReaxFF parameters used were those developed by Vasenkov et al. [189]. Systems were visualised using OVITO [315] and VESTA [316] software.

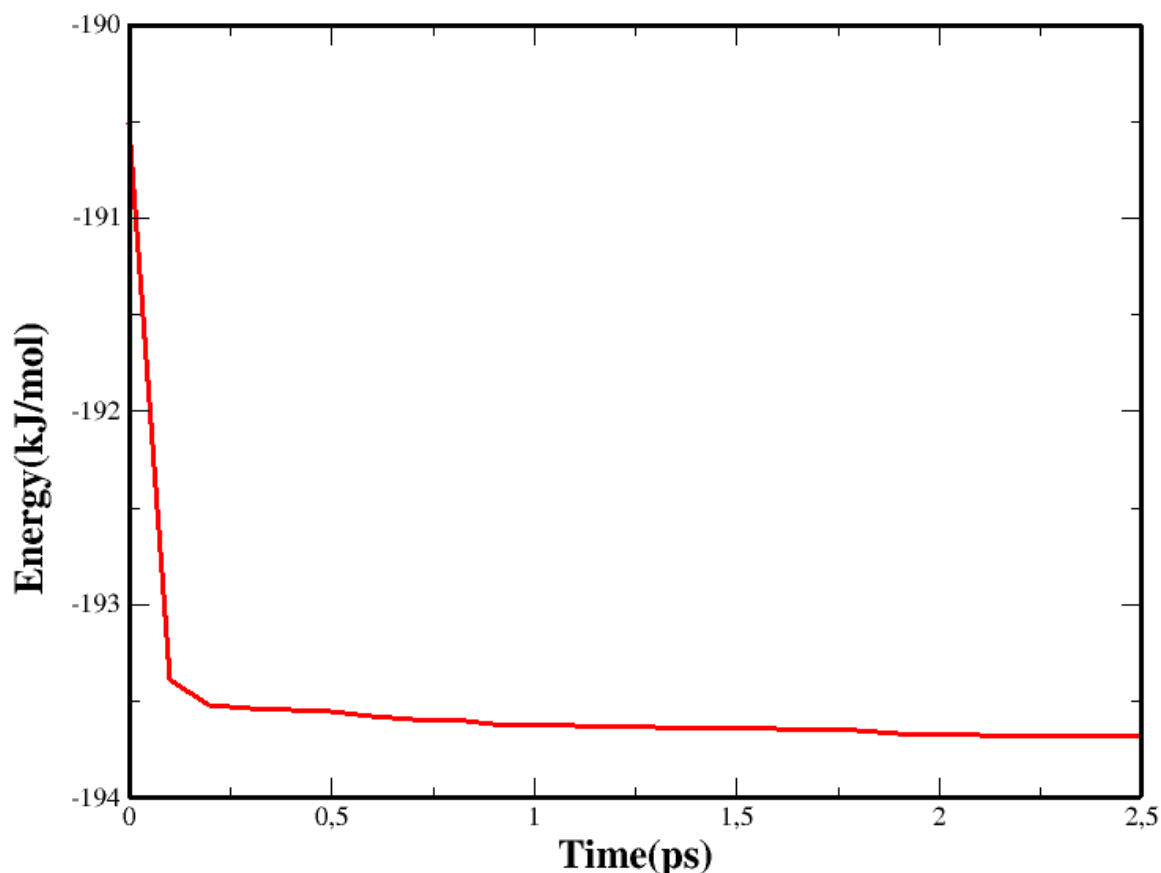


Figure 68: The change in potential energy during the energy minimisation.

6.3 Results and discussion

6.3.1 Validation of force field parameters

To validate the ReaxFF force field parameters in this study, we calculated the bond dissociation curves of two methyl palmitate bonds (C1-C2 and C14-C15) using DFT and ReaxFF. The results are presented in Figure 69(a & b). ReaxFF calculated the minimum energy equilibrium bond distances for C-C bonds was found to be 1.57 Å, which is consistent with DFT. At shorter

distances, the energy curves also have similarities. However, deviations are observed beyond distances of 1.6 Å [136,317].

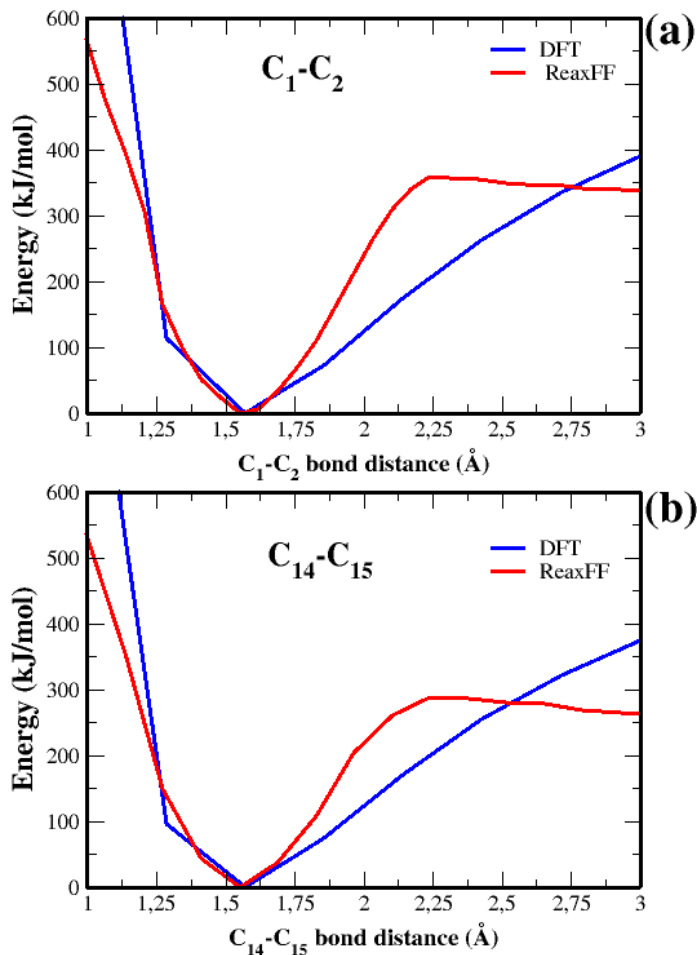


Figure 69: The plots of DFT (B3LYP/6-311+G (d, p)) calculated (blue line) and ReaxFF (red line) potential energy scans for dissociation of C₁-C₂ (a) and C₁₄-C₁₅ (b) bonds of the methyl palmitate.

Bond dissociation enthalpies were calculated along the major methyl palmitate chain (refer to Figure 66 for atom numbering) using parameters derived by Vasenkov et al. [318] and DFT using equation 6.2, and the results are shown in Figure 70(a).

$$\Delta H_{Tot} = \Delta H_{MP} - (\Delta H_1 + \Delta H_2) \quad 6.2$$

In equation 6.2, ΔH_{Tot} is the total enthalpy for the dissociation, and ΔH_{MP} is the enthalpy of the optimised methyl palmitate molecule. The ΔH_1 and ΔH_2 are the enthalpy of optimised fragments respectively.

For bonds 1-13, the bond enthalpies computed using DFT and ReaxFF are quite similar. However, DFT calculated bond enthalpies were higher than ReaxFF for bonds 14 to 17. Bonds 14 and 15 are C-C bonds closer to the carbonyl group, whereas bonds 16 and 17 are C-O bonds. As a result of the electronegative oxygen atoms, these bonds become more polarized. Within cut-off distances of about 2.6 Å, the dissociation curves of ReaxFF tend to agree with DFT [317]. Thus, these bonds are more polarized due to the electronegative oxygen atoms. In general, the dissociation curves of ReaxFF tend to agree with DFT within cut-off distances of about 2.6 Å [317], which is shorter than the distances used in the calculation of bond enthalpies. The disagreement seems to be worsened in the case of polar bonds. Another possible explanation is that when molecules in this region undergo bond dissociation, they produce highly reactive and unstable radicals. These radicals have a greater tendency to react with different atoms of the dissociating fragments, resulting in slightly lower dissociation energy. In general, the obtained results are reasonable, indicating the reliability of using ReaxFF to investigate the decarboxylation of FAMES. The energies calculated by DFT are also consistent with Meng and coworkers', findings for methyl linoleate [184]. The dissociation energies of the C-H bond, as shown Figure 70(b), also exhibit a strong correlation between DFT and ReaxFF. The energy difference between the two methods is less than 23 kJ/mol, which is acceptable [180]. All energies observed for C-H dissociation along the methyl palmitate chain were higher than those in Figure 70(a), making bond initiation via C-H cleavage unfeasible.

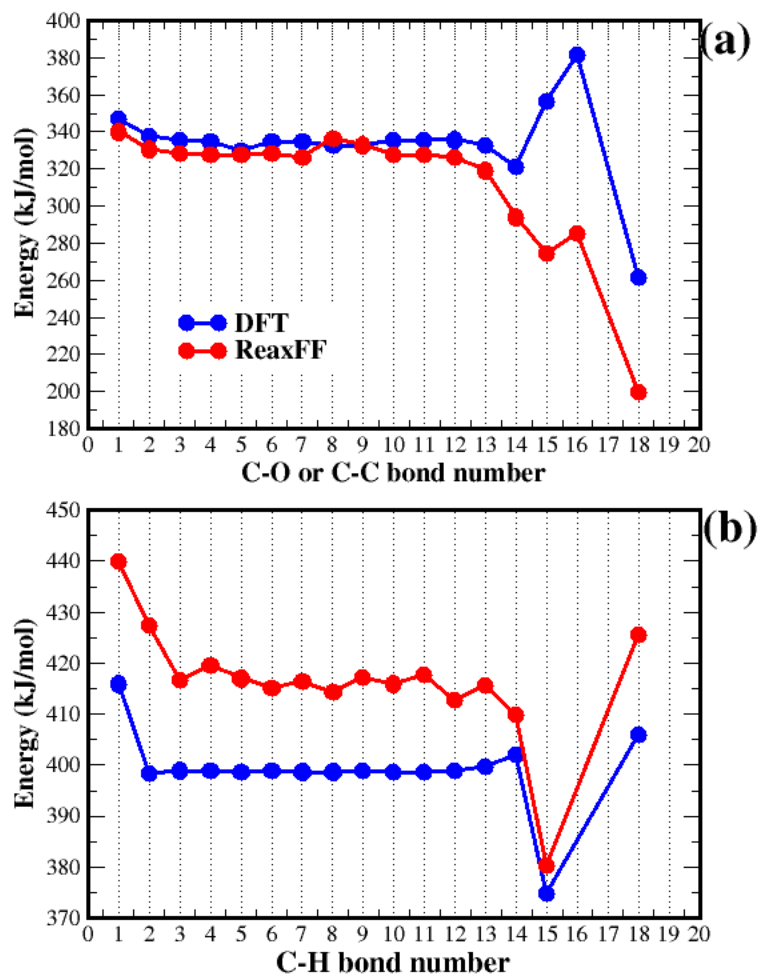


Figure 70: Comparison of DFT and ReaxFF calculated bond enthalpies of bonds along the main chain of methyl palmitate (a) C-H or C-O bonds and C-H bonds (b). For C-C and C-O bonds, the bond label is such that bond i is a bond between atoms i and $(i+1)$. For C-H bond labels, bond i is the bond between atom i and a H atom connected to it.

6.3.2 Effect of thermostats and timestep

ReaxFF simulations are known to be sensitive to the selected thermostat algorithm and molecular dynamics time step[319]. For this reason, the effect of these two parameters on the results was preliminarily investigated. Additionally, poor equilibration of systems can lead to chemically unfeasible fragmentations which can easily lead to misinterpretation of results. Therefore, system stability against fragmentation due to non-equilibration was monitored. The most widely used

thermostats in ReaxFF simulations are Berendsen and Nosé-Hoover[192,193,267]. The influence of the thermostat on the rate of ethene production from methyl palmitate over the β -NiMoO₄ (021) catalyst is depicted on Figure 71. The results show that the choice of thermostat does not affect ethene production, except for small variations observed between 5-18 ps[319].

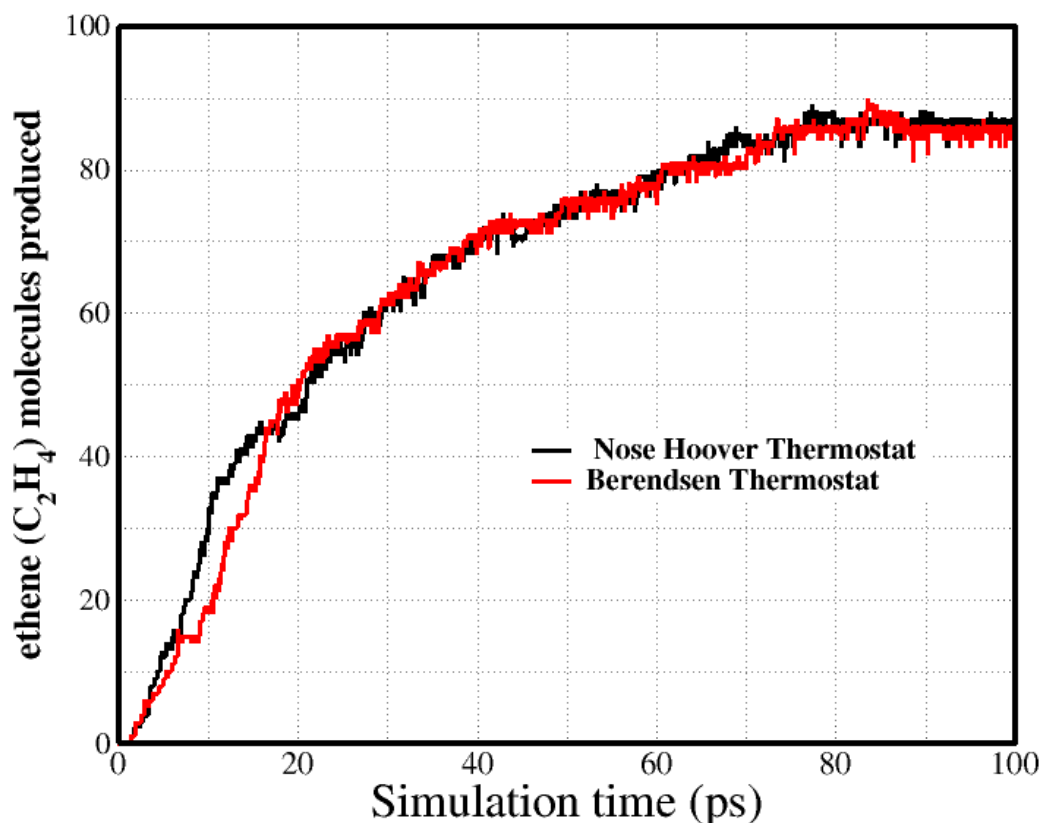


Figure 71: The effect of thermostat on the evolution of ethene. Molecular dynamic simulations were conducted at 2500K with 0.1 fs timestep on a β -NiMoO₄ (021) catalysed system.

Time step is one of the most important parameters in molecular dynamics[320]. With regard to molecular dynamics time step, if it is too large, the system's total energy will not be conserved and will likely increase over the duration of the simulation[319]. The time step required to achieve reliable results with ReaxFF is different from the one used in conventional force fields. This is because ReaxFF involves bond breaking and formation, which causes non-linear forces between the interacting atoms, unlike traditional force fields. Traditional force fields use harmonic bond stretches, which exhibit linear force–distance relationships for all deformation

magnitudes[319,321]. Additionally, ReaxFF employs the charge equilibration mechanism to handle charge transfer between atoms during reactions[179,183]. These factors have an influence on the time step selection. This led to the investigation of the effect of time steps on the evolution of products. The investigation centred on the most commonly reported time steps for hydrocarbon reactions, specifically 0.1 fs and 0.25 fs[140,184]. The evolution of carbon dioxide and ethene at 1500K on the β -NiMoO₄ (021) surface at these time steps is depicted in Figure 72(a & b). The results show that the smaller time step produced fewer molecules of C₂H₄, and CO₂ compared to the higher time step of 0.25fs. Using a higher time step led to rapid fragmentations and made it difficult to monitor products of interest. This was particularly noticeable when using a time step of 0.25fs, especially in the case of CO₂. After 60ps the amount of CO₂ started decreasing, indicating that it was fragmenting[322]. The simulations in this chapter were conducted using the 0.1fs time step.

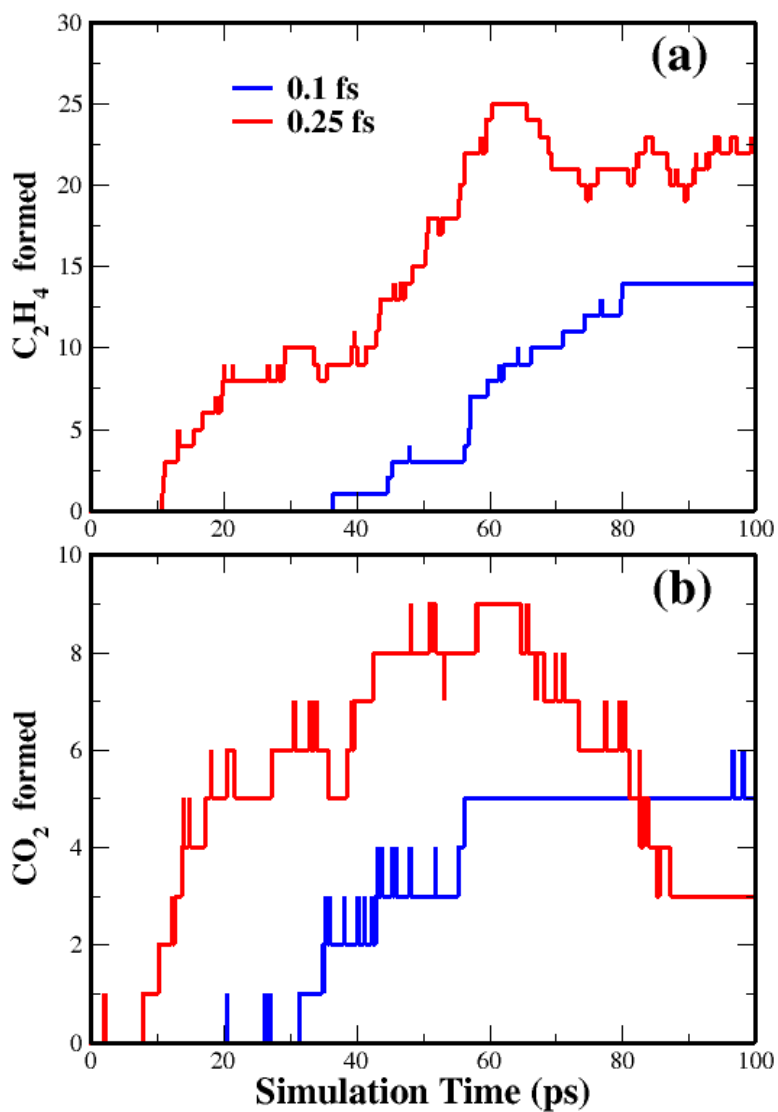


Figure 72: The effect of time step on the evolution of ethene (a) and carbon dioxide (b). Simulations were conducted at 1500K on the β -NiMoO₄ (021) catalysed system.

6.3.3 Stability of methyl palmitate

To rule out unfeasible reactions, the number of molecules of methyl palmitate that remained intact as a function of time were monitored and the results are presented in Figure 73. The methyl palmitate molecules are seen to be stable even at 1200K. For non-equilibrated systems, spurious fragmentation would occur even at low temperatures. The reactions and conversion of MP to products only started at 1300K, in catalysed systems and at 1500K in uncatalysed systems. This is expected since the increase in kinetic energy eventually leads to fragmentation.

We note that in experimental conditions conversion to products starts at lower temperatures. However, the amount of time required to observe that in molecular dynamics is not feasible. Thus elevated temperatures were used to speed up the reaction[305].

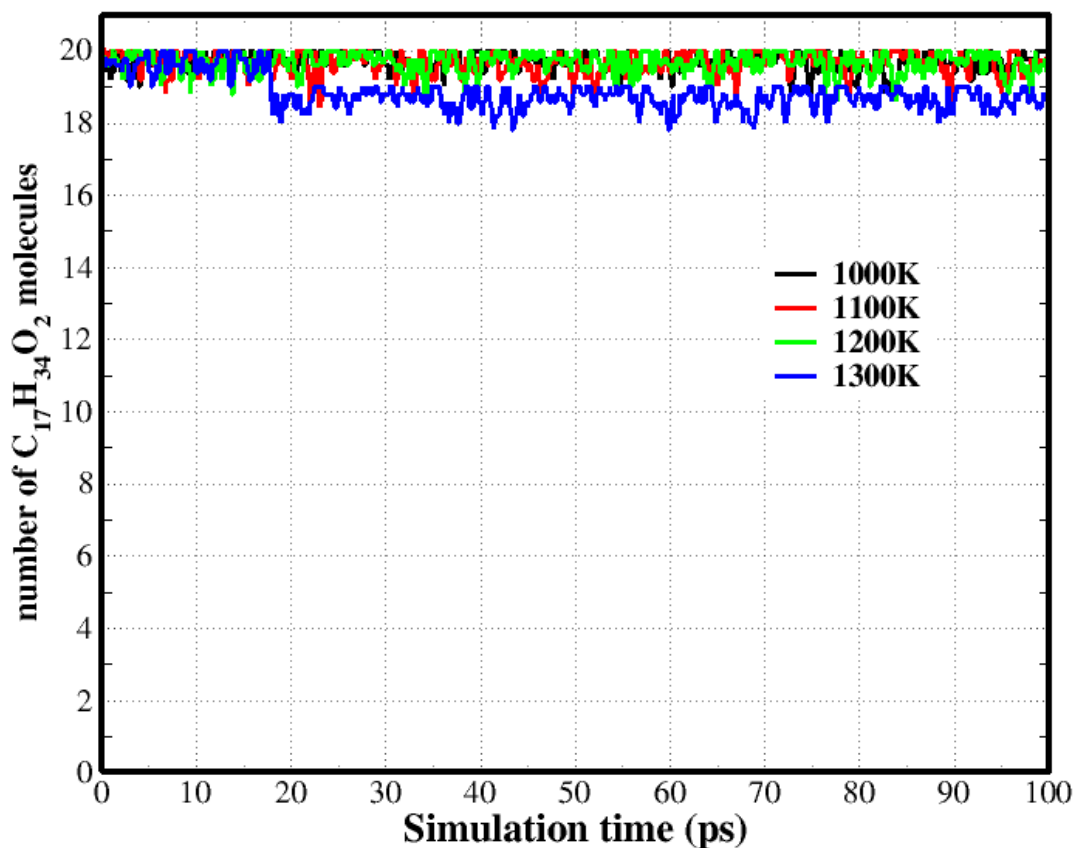


Figure 73: Number of methyl palmitate molecules as a function of the simulation time at different temperatures. This was conducted on a β -NiMoO₄ (110) catalyst.

6.3.4 Comparison of catalyzed and un-catalyzed reactions

Experimental studies have shown that the pyrolysis of fatty acid methyl esters at temperatures ranging from 300-1300°C results in the formation of various products, including ethene and carbon dioxide [323,324]. Furthermore, a ReaxFF study conducted by Sui et al. on the pyrolysis of methyl linoleate demonstrated that the results agreed with experimental data[184]. One of the major products of pyrolysis of methyl palmitate is ethene. The effect of the catalyst in the

decarboxylation of methyl palmitate was studied by comparing, the amounts of C_2H_4 generated with and without the catalyst. For simulations without a catalyst, the system was prepared as stated above but without the slab atoms. The ReaxFF molecular dynamic simulations were then carried out, with the methyl palmitate molecules in both systems gradually heated from 600K to 3000K at a heating rate of 10K/ps. The amount of C_2H_4 produced as a function of temperature is shown in Figure 74. The formation of C_2H_4 starts at a higher temperature without a catalyst (black line) compared to catalysed systems. With the exception of Ni_3Mo catalysed system (blue line) the total amount of C_2H_4 produced under the presence of catalyst was almost twice the amount produced without a catalyst. It is clear in this case that the presence of the catalyst speeds up the production of ethene.

When comparing the amount of C_2H_4 formed in different systems, there are minor differences that are observed. The earliest formation of C_2H_4 is observed in the β - $NiMoO_4$ catalysed system at 1200K. Only small quantity of C_2H_4 is observed at this temperature. We also observed rapid formation in the Ni_3Mo catalysed system. Here an initial rapid formation is observed until a maximum is reached at around 2200K, which is then followed by a decrease in the amount formed, indicating that it is being converted to other compounds at high temperature. In the α - $NiMoO_4$ and β - $NiMoO_4$ catalysed systems, an increase in temperature causes an increase in the amount of C_2H_4 formed, with the highest amount observed in the β - $NiMoO_4$ catalysed system[305].

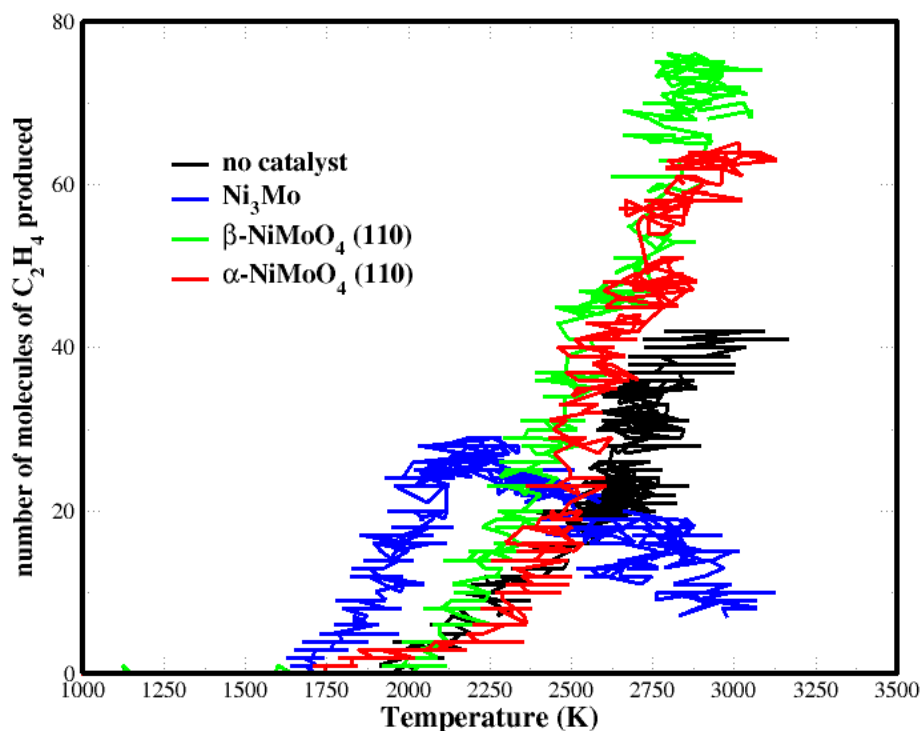


Figure 74: Formation of C_2H_4 systems with and without catalyst

6.3.5 Major products evolution as a function of time

The analysis of the ReaxFF trajectory shows that the first products to be formed with or without a catalyst are $CH_3^\bullet$ and $C_{16}H_{31}O_2^\bullet$ radicals. The weakest bond, with bond enthalpy of 207kJ/mol and 261kJ/mol from ReaxFF and DFT respectively, is the O-CH₃ bond (Figure 70(a)). This shows that the reaction is most probably initiated by the cleavage of this bond which leads to the generation of $CH_3^\bullet$ and $C_{16}H_{31}O_2^\bullet$ radicals. Because of its high enthalpy energy, the (C=O)-O is eliminated as the reaction initiation step. Once formed, the $C_{16}H_{31}O_2^\bullet$ radical is further fragmented leading to the formation of both stable and unstable products. The stability of the products is determined from the comparison of their production rate and consumption rate[138]. The unstable products included longer olefins and radicals which decomposed as the simulation progressed, while shorter olefins and carbon dioxide whose composition increased with simulation time were considered stable. Figure 75(a-f) show the evolution of carbon dioxide (CO₂) and some of the olefins produced against simulation time. Ethene (C₂H₄) and CO₂ are

produced in large quantities, with CO₂ being produced earlier and at lower temperature. C₁₆H₃₁O₂[•] radical fragmented to give CO₂ and C₁₅H₃₁[•] radical in all systems[137]. C₂H₄ is produced in large quantities which is indicative of its several production channels which include the decomposition of longer olefins and hydrocarbon radicals[140,184,325]. Comparatively, more of both CO₂ and C₂H₄ are produced when NiMoO₄ is used as a catalyst compared to when Ni₃Mo are used. The order of amount C₂H₄ produced obtained is α -NiMoO₄ (021) > β -NiMoO₄ (110) > α -NiMoO₄ (110) > β -NiMoO₄ (021) > Ni₃Mo (101). When it comes to the formation of CO₂ the highest amount is still observed when using NiMoO₄ catalysts. Other stable products observed included propene (C₃H₆) and butene (C₄H₈) which were produced at later stages of the simulation, with the β -NiMoO₄ (110) and α -NiMoO₄ (021), catalysts having a higher selectivity of both compared to α -NiMoO₄(110), β -NiMoO₄ (021) and Ni₃Mo catalyst. These two alkenes were not observed in the uncatalyzed system. Longer olefins from C5-C15 were also produced, however, these were not stable as they fragmented to shorter olefins as the simulation progressed[140,185].

The phases of 110 NiMoO₄ phases expose atoms of Ni, Mo, and O, as shown in Figure 65(a & c). The superior performance of the β -NiMoO₄ (110) catalyst as compared to other catalysts can be attributed to the pores between the atoms[293,326]. This observation is consistent with what was observed when the same catalyst was used in the oxygen production from urea[327]. The (021) planes exhibit higher levels of porosity as compared to the (110) planes (Figure 65) which possibly leads to increased adsorption sites. As shown in Figure 76(a) the introduction of a catalyst favors the formation of shorter hydrocarbons in contrast to experimental observations[125,291]. The uncatalyzed system has the highest yield of longer hydrocarbons at 21%. The β -NiMoO₄ has the highest selectivity of 11% towards the formation of long-chain alkenes compared to 6% and 2% respectively for α -NiMoO₄ and Ni₃Mo alloy. The introduction of catalysts promotes the cracking of long hydrocarbons, resulting in shorter chains. The formation of olefins is mostly favoured in the hydrogen free environment than alkanes[328]. Experimentally, the specific surface area of α -NiMoO₄ is around 50.26 m²/g, while that of β -NiMoO₄ is 116.98 m²/g. This high specific surface area in the case of β -NiMoO₄ indicates that a large amount of active surface is accessible for reactions and also shows greater adsorption capacity [327] which is in agreement with our observations.

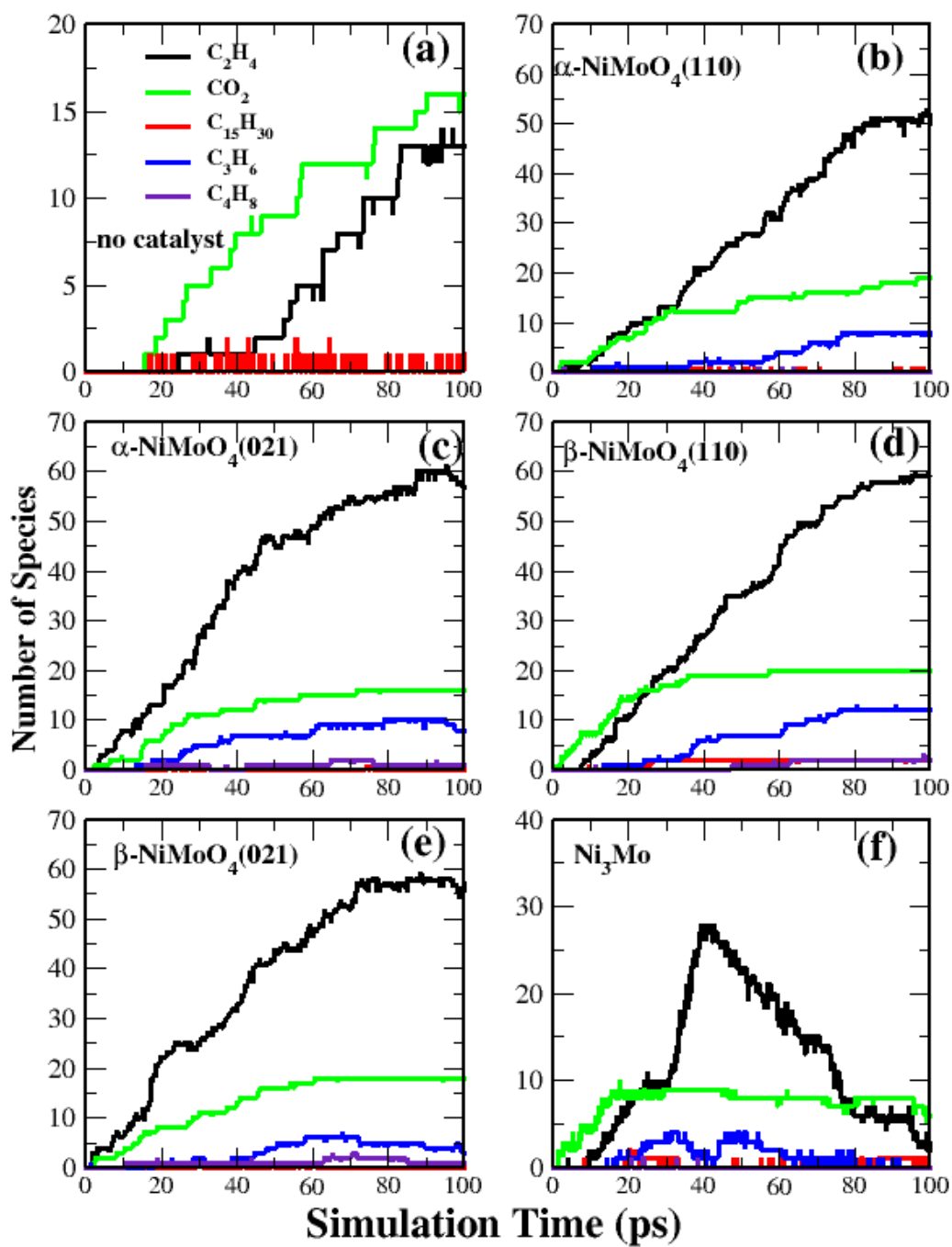


Figure 75: Time evolution of stable products at 2000K. (a) uncatalyzed reaction (b) $\alpha-NiMoO_4$ (110), (c) $\alpha-NiMoO_4$ (021) (d) $\beta-NiMoO_4$ (110) (e) $\beta-NiMoO_4$ (021) and (f) Ni_3Mo (101), catalysed reactions.

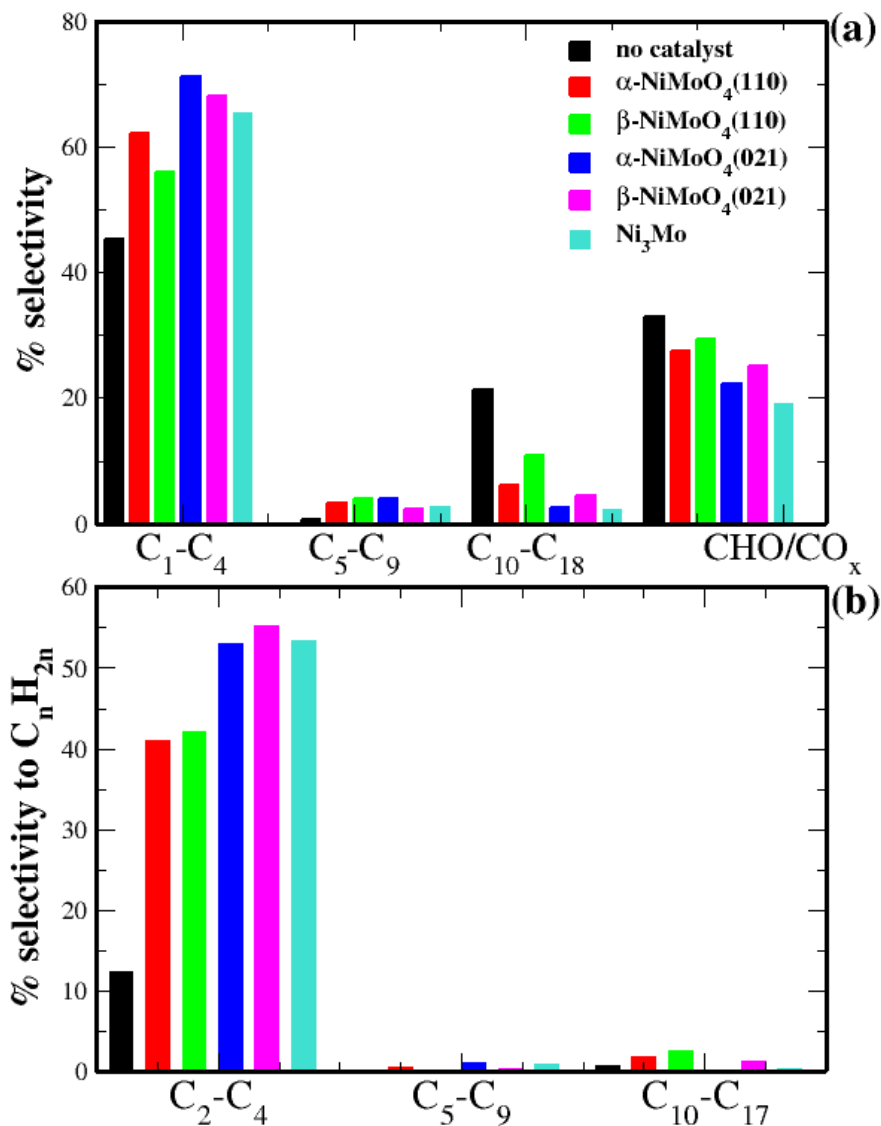
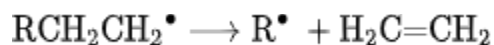


Figure 76: Product distributions (a) selectivity towards hydrocarbons, (b) selectivity towards olefins at 2000K.

Another noticeable difference is the accumulation of C₂H₄ at 2000K. In uncatalyzed, α -NiMoO₄ and β -NiMoO₄ catalyzed systems, we observe a gradual increase in the amount of ethene generated. The generation of this gas is mainly through β -scission reactions of both alkane and alkene radicals[138] (equation 6.3), and these reactions were found to be dominant hence high quantity of ethene was observed.



6.3

On the other hand, in the Ni₃Mo catalysed system the amount of ethene increased until around 40 ps where a decrease in the amount was observed (Figure 75(f)) indicating that it is being consumed. A plot of the evolution of C₂H₄, C₂H₂ and H₂ species with time is shown in Figure 77. It is evident from the figure that C₂H₂ only appeared in the system after the concentration of C₂H₄ started to decrease, indicating that C₂H₂ is being formed from C₂H₄. The H₂ gas (green line) also started forming about the same time as C₂H₂ showing that it is also formed from the decomposition of ethene.



Another important product of decarboxylation is the CO₂ molecule. The evolution of this species in Ni₃Mo catalysed reaction shows that the amount of CO₂ plateaus after only 10 molecules were produced. This is in contrast to NiMoO₄ catalysed systems where almost all of the 20 molecules of MP were decarboxylated to form CO₂ molecules. Analysis of trajectories showed that MP adsorbed on the catalyst surface, on the Ni atom via the O atom, and some of the adsorbed molecules were not desorbed within the 100ps which resulted in fewer CO₂ molecules formed. The other observation was the formation of carbon monoxide (CO) which has been observed before in the catalytic pyrolysis of triglycerides[145]. This molecule was formed albeit in small quantities at 2000K. Its formation was only observed when the amount of CO₂ started decreasing (Figure 78). The formation of CO has been found to give rise to the formation of water due to the reduction of CO₂ by hydrogen which is not desirable in green diesel production[329,330]. In this investigation, water was only formed at temperatures greater than 2000K.

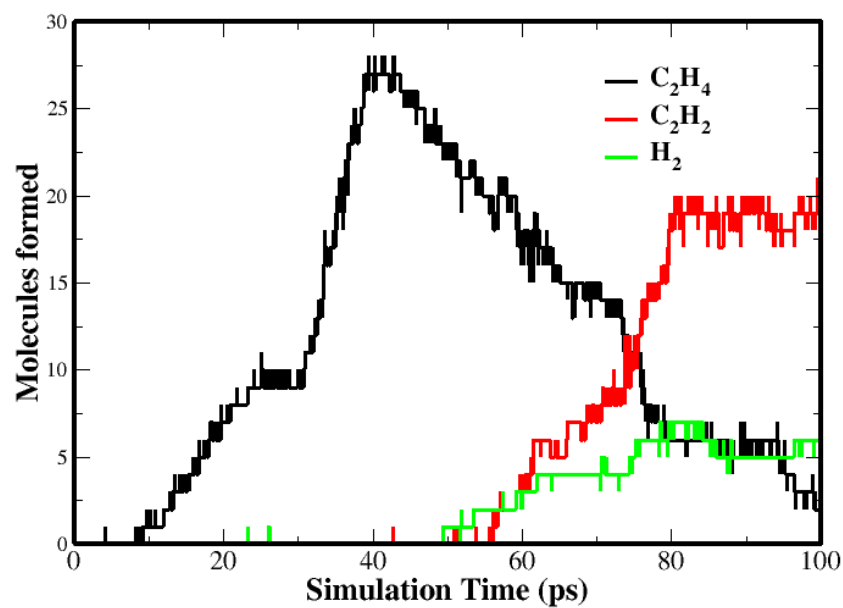


Figure 77: Evolution of C_2H_4 , C_2H_2 and H_2 as a function of time in the Ni_3Mo catalysed system at 2000K.

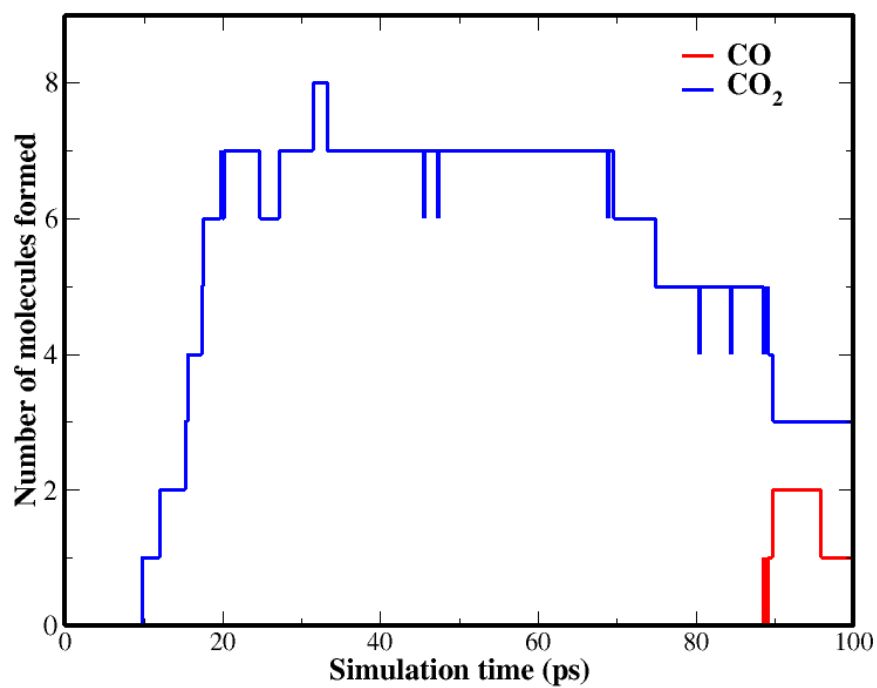


Figure 78: Evolution of CO_2 and CO as a function of time in the Ni_3Mo catalysed system at 2000K.

6.3.6 Formation of Major Radicals

Presented in Figure 79 is the accumulation of the major radicals as the simulation progresses. Beside $\text{CH}_3^\bullet$ and $\text{C}_{16}\text{H}_{31}\text{O}_2^\bullet$ other major radicals produced include $\text{C}_{15}\text{H}_{31}^\bullet$ and $\text{C}_2\text{H}_5^\bullet$. Without a catalyst, the accumulation of $\text{CH}_3^\bullet$ increases as the simulation progresses which shows that it does not get used up or converted to any products[138]. In the same system, the amount of $\text{C}_{16}\text{H}_{31}\text{O}_2^\bullet$ is slowly increasing until around 90ps where it starts decreasing, which is indicative of slow consumption[186]. In catalysed systems, we observe an initial increase in the accumulation of these two radicals until a maximum is obtained. When comparing the consumption of both radicals in the catalysed system, a faster decay is observed in Ni_3Mo as a catalyst compared to the other two catalysts. The surface exposed 101 planes of Ni_3Mo exposes Ni atoms mostly unlike the NiMoO_4 catalysts which expose Ni, Mo and O atoms (Figure 65). The higher composition of nickel on the surface of Ni_3Mo may be the reason for the fast adsorption of radicals, which are later desorbed as products. This, in turn, leads to a higher conversion of radicals into new products, making it more active. The rate of decay of radical $\text{C}_{16}\text{H}_{31}\text{O}_2^\bullet$, is in the order $\text{Ni}_3\text{Mo} > \beta\text{-NiMoO}_4(021) > \beta\text{-NiMoO}_4(110) > \alpha\text{-NiMoO}_4(110) > \alpha\text{-NiMoO}_4(021)$.

Sancheti et al., proposed that the initial adsorption of FAME occurs on metal centre without being specific about the nature of the metal[125]. Closer inspection of ReaxFF trajectories reveals that the initial adsorption occurs on the Ni atom. Once formed, the $\text{CH}_3^\bullet$ radical is expected to combine with the adsorbed $\text{H}^\bullet$ radical to form CH_4 (equation(6.5)[125]. Even though the $\text{CH}_3^\bullet$ and $\text{H}^\bullet$ radicals are formed in high quantities, their collision appears not to be frequent looking at few CH_4 molecules formed. The yield is less than 1% in all catalysed systems at 2000K.



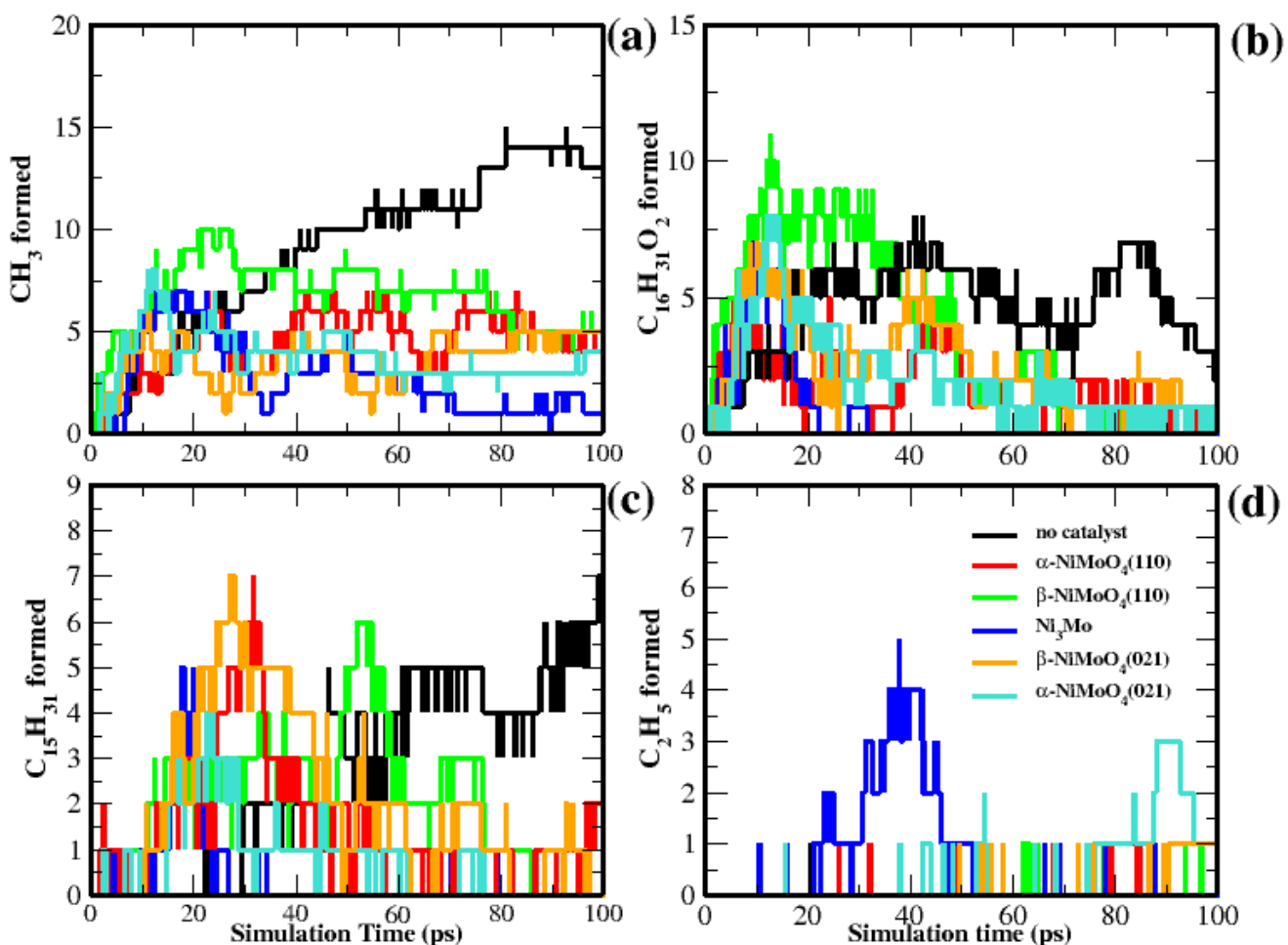


Figure 79: Formation of radicals $\text{CH}_3^\bullet$, $\text{C}_2\text{H}_5^\bullet$, $\text{C}_{15}\text{H}_{31}^\bullet$, $\text{C}_{16}\text{H}_{31}\text{O}_2^\bullet$, on catalysed and uncatalyzed systems at 2000K.

The evolution of $\text{C}_{15}\text{H}_{31}^\bullet$ at 2000K is presented in Figure 79(c). Just like $\text{CH}_3^\bullet$ and $\text{C}_{16}\text{H}_{31}\text{O}_2^\bullet$ the consumption of this radical is low in the uncatalyzed system, indicative of slow reaction. For catalysed systems there is a rapid increase in the amount produced with the α -NiMoO₄(110) (red line) and β -NiMoO₄(021) (orange line) producing the most. This is then followed by a rapid decrease. The order of consumption being in the order $\text{Ni}_3\text{Mo} > \alpha\text{-NiMoO}_4(021) > \beta\text{-NiMoO}_4(110) > \beta\text{-NiMoO}_4(021) > \alpha\text{-NiMoO}_4(110)$. In Ni_3Mo catalysed system all the produced $\text{C}_{15}\text{H}_{31}^\bullet$ is used up by 35ps and in $\alpha\text{-NiMoO}_4(021)$ is used up by 76ps, while in $\beta\text{-NiMoO}_4(110)$ it is used up by 90ps. Three scenarios can be used to explain these observations. First, some of the $\text{C}_{15}\text{H}_{31}^\bullet$ gets adsorbed on the catalyst slab, with the Ni_3Mo expected to experience more adsorption.

Comparison of snapshots of the adsorbed species at 35ps shows that there are more species adsorbed on Ni₃Mo surface than in the other two catalysts (Figure 80(a)). Secondly, C₁₅H₃₁[•] can lose an H[•] radical to form pentadecane C₁₅H₃₀ (equation 6.6) which is mostly favoured in hydrogen free environment[125].



The percentage yield of this product was around 5% in uncatalyzed, α-NiMoO₄ (110), β-NiMoO₄(021) catalysed systems and it was 10%, 11% and 12% in β-NiMoO₄ (110), α-NiMoO₄ (021), and Ni₃Mo catalysed systems respectively (Figure 81). The reaction with a hydrogen radical to form, C₁₅H₃₂, which is our target green diesel product (equation 6.7), is another channel.



This product was only observed in Ni₃Mo catalysed reactions. This catalyst seems to be the most active. However, it is not selective as the selectivity of less than 1% was observed. The C₁₅H₃₁[•] radical can also undergo another β-scission decomposition to give C₁₃H₂₆ olefin and C₂H₅[•] radical.



The evolution of the C₂H₅[•] radical is presented in Figure 79(d). It is observed in small quantities in uncatalyzed, α-NiMoO₄ and β-NiMoO₄ catalysed systems. However, in Ni₃Mo catalysed system a gradual accumulation followed by a decay after 40ps is observed.

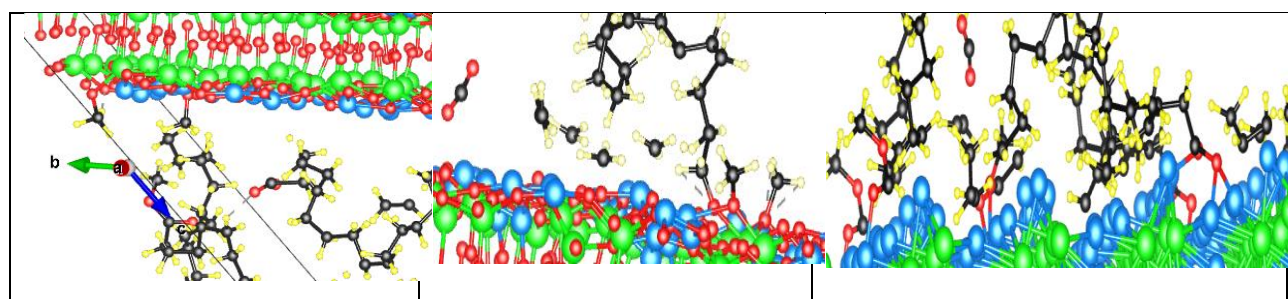


Figure 80: Snapshots of the surfaces at 35ps. (a) α -NiMoO₄, (b) β-NiMoO₄ and (c) Ni₃Mo.

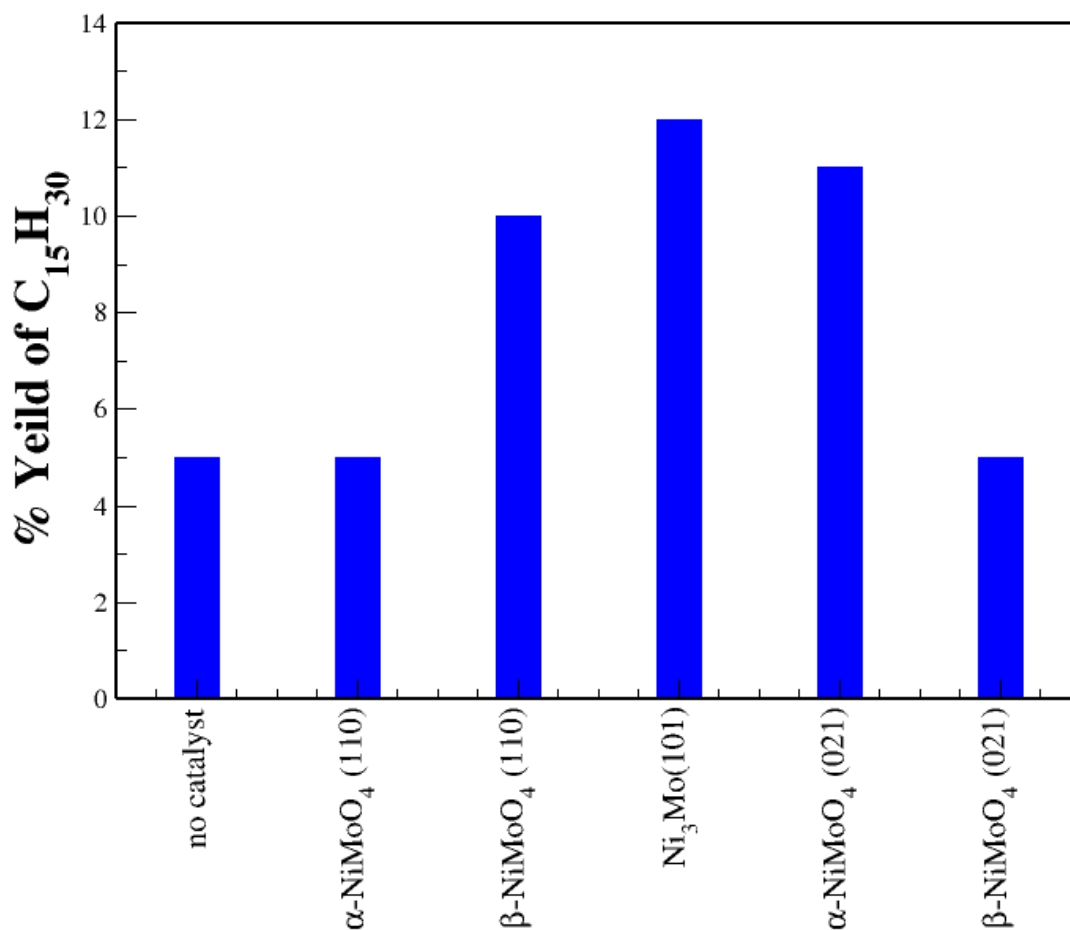


Figure 81: Percentage yields of pentadecene (C₁₅H₃₀) on different catalyst surfaces.

6.3.7 Effect of temperature

Figure 82 shows the conversion or decomposition of methyl palmitate (MP) as a function of time over 110 planes of α-NiMoO₄ and β-NiMoO₄, and the (101) plane of Ni₃Mo catalysts and uncatalyzed system. It is also clear that an increase in temperature results in an increase in the amount of MP converted to products[136,138]. The highest conversions are observed in the Ni₃Mo catalysed system at all temperatures. At 2000K (green line) the highest conversion is achieved by Ni₃Mo where all MP are used up by 35ps, while in the β-NiMoO₄ catalysed system the complete conversion is achieved at 60ps and for the α-NiMoO₄ it was after 80ps. For the uncatalysed reaction, 100% conversion is not achieved within 100 ps.

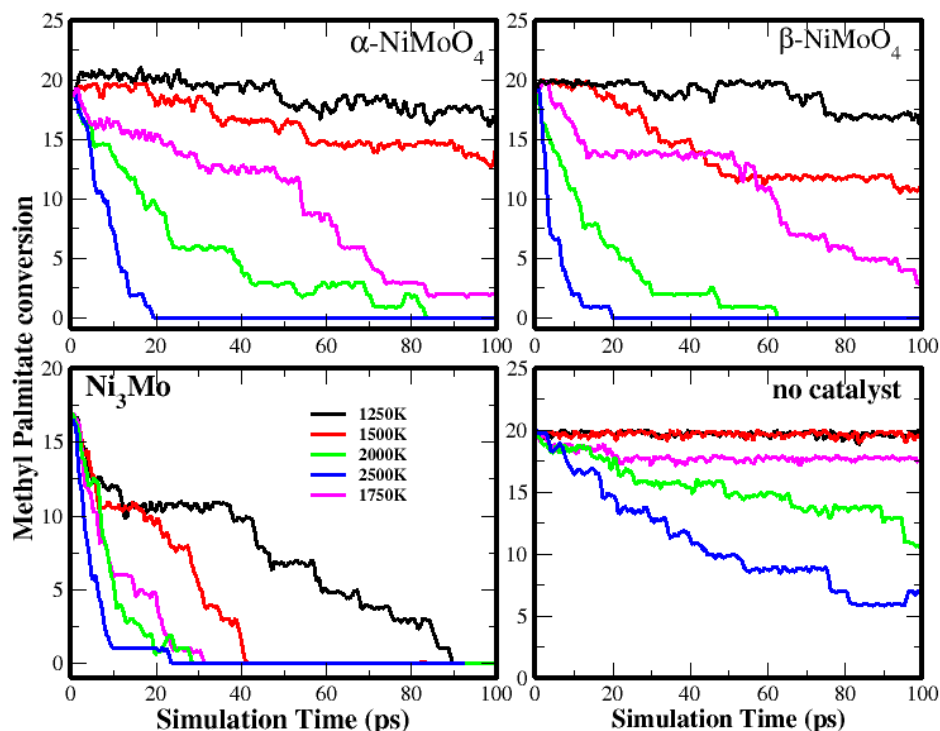


Figure 82: The depletion of methyl palmitate as a function of time.

The evolution of products formed in large quantities was followed at different temperatures to investigate the effect of temperature on their formation. Figure 83 and Figure 84 show the formation of CO₂ and C₂H₄ as a function of time. Formation of CO₂ is observed at a lower temperature of 1250K while the earliest detection of C₂H₄ was after at 1500K. The amount of CO₂ produced from the initially added 20 molecules of MP, increases with temperature, 20 molecules are produced at 2500K while only one molecule was produced at 1250K. In Ni₃Mo catalysed system the MP initially adsorbed on the surface Ni atoms via O atoms. This appears to be strong making the desorption of products very difficult, especially at low temperatures. This causes fewer molecules of CO₂ to be formed. At elevated temperatures, CO is formed. Its quantity increases as CO₂ decreases, indicating the conversion of some CO₂ to CO. Figure 85 is a snapshot of the catalyst slab at 100ps for the simulation at 2500K, the bonds between O and Ni can be observed. Although few free molecules are observed, it must be noted that the rate of formation of CO₂ still increases with temperature as expected (Figure 83(d)). In the case of C₂H₄ the amount increases with increasing temperature as shown in Figure 84. At elevated temperatures longer olefins and alkanes decompose, with ethene being the predominant

product[136,140,185]. The Ni_3Mo catalysed reaction is slightly different from others as shown in Figure 84(f) with free C_2H_4 accumulating to a maximum and then dropping again due to adsorption on the catalyst surface and being converted to acetylene and hydrogen gas[138,186]. The total number of fragments formed at different temperatures were also monitored and results are presented in Figure 86. At 1250K the highest number of fragments are observed for the 021 catalysed systems. As expected, fragmentation also increases with temperature[185]. At the 2000K less cracking is observed in Ni_3Mo and uncatalyzed systems. Increase in temperature in our situation, is not advantageous because it lowers the output of long-chain green diesel.

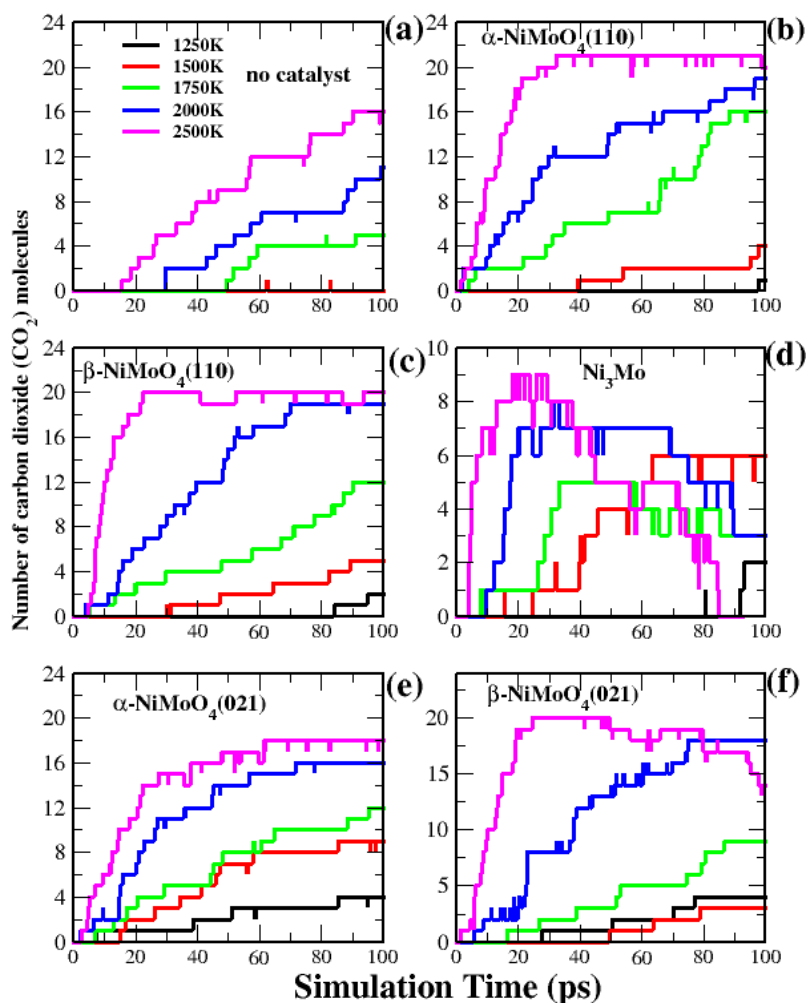


Figure 83: Amount of CO_2 molecules formed as a function of time. (a) uncatalyzed reaction (b) $\alpha\text{-NiMoO}_4$ (110) (c) $\beta\text{-NiMoO}_4$ (110) (d) Ni_3Mo (101), (e) $\alpha\text{-NiMoO}_4$ (021) and (f) $\beta\text{-NiMoO}_4$ (021) catalysed reactions.

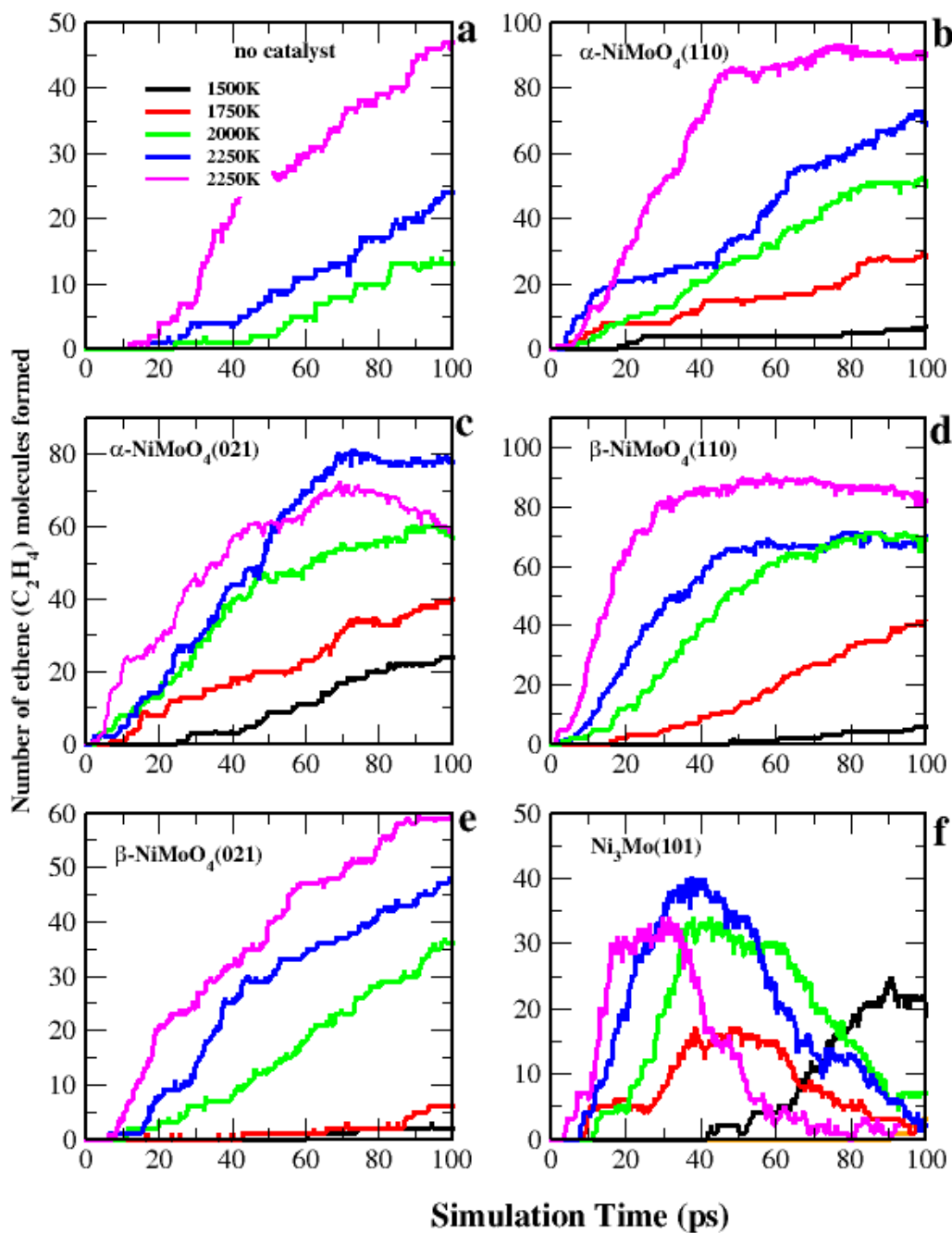


Figure 84: The number of ethene (C_2H_4) molecules that are formed as a function of time in the (a) uncatalyzed reaction (b) $\alpha-NiMoO_4(110)$ (c) $\alpha-NiMoO_4(021)$, (d) $\beta-NiMoO_4(110)$ (e) $\beta-NiMoO_4(021)$ and (f) $Ni_3Mo(101)$ catalysed reactions.

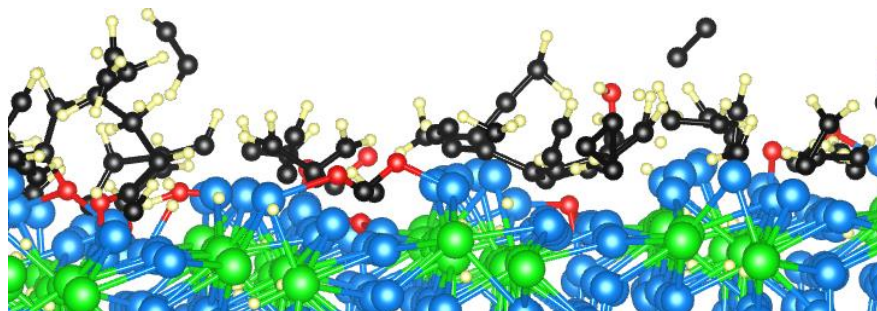


Figure 85: The snapshot of the catalytic slab of Ni_3Mo at 2500K at 100ps simulation. Key- blue- Ni atoms, green-Mo, red- O, black-C and Yellow -H

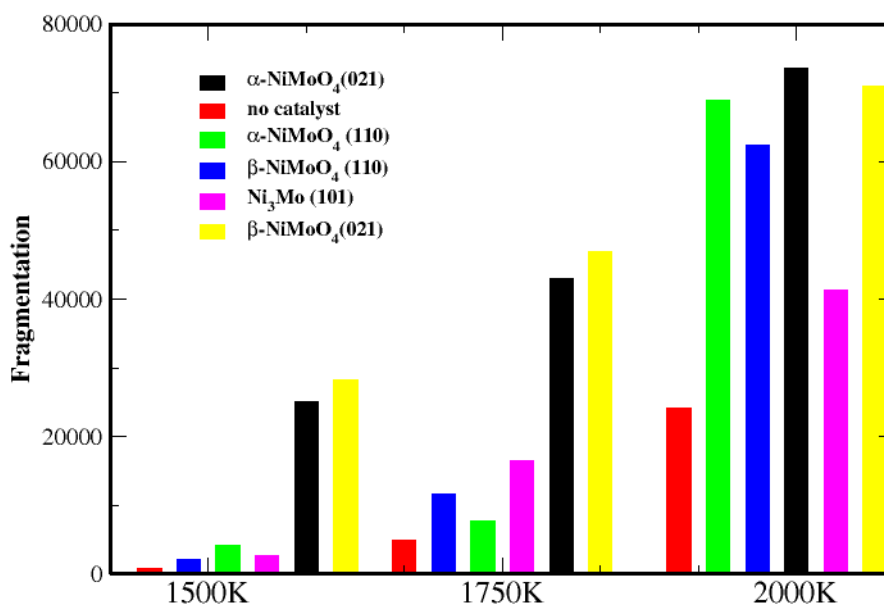


Figure 86: The number total number of fragments formed at different temperature in different surfaces.

6.3.8 Kinetics

To investigate the kinetics of the decarboxylation of MP over the NiMoO_4 catalysts, Ni_3Mo and uncatalyzed system, simulations were carried out at temperatures ranging from 1250K-2500K. Adsorption of reactant MP varied across catalysts, making conversion tracking difficult. As a result, instead of monitoring MP conversion, we chose to monitor CO_2 formation, which follows equation 6.9.



At the beginning of the simulation, the number of CO₂ molecules is zero. As the simulation progresses, the number increases, and if the reaction goes to completion, the maximum number of CO₂ produced from the added 20 MP molecules is 20. The conversion of MP, X_t , at time (t), is related to the amount of CO₂ produced via equation 6.10.

$$X_t = \frac{N_o - N_t}{N_o} \quad 6.10$$

Where N_t is the number of molecules of CO₂ at the time (t) and N_o is the maximum possible number of CO₂ molecules, which in this case is 20. Following the method proposed by Sancheti et al., the first-order rate constant k , can be obtained via a plot of equation (6.10) [125,331,332]. Here a plot of $-\ln(1 - X_t)$ vs t was made as a function of time (Figure 87) [138,184,185,333].

$$-\ln(1 - X_t) = kt \quad 6.11$$

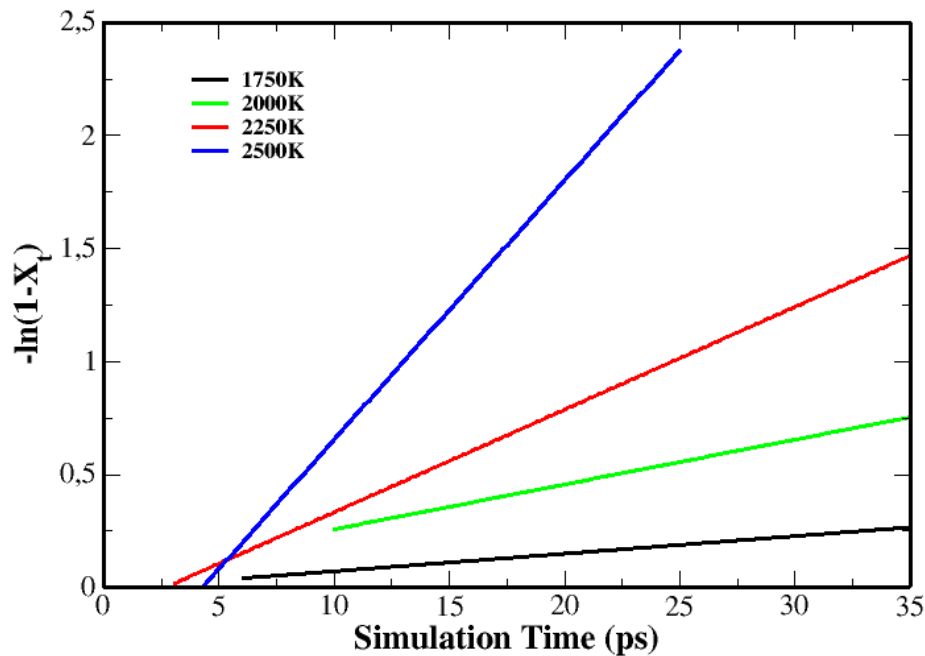


Figure 87: A sample first-order plot for the formation of carbon dioxide at different temperatures for a system catalysed by β -NiMoO₄ (021).

With values of the rate constant at different temperatures (T), the activation energy, E_a , was obtained from the Arrhenius equation (equation 6.12)

$$\ln k = \ln A - \frac{E_a}{RT} \quad 6.12$$

Where A is the pre-exponential factor. Presented in Figure 88 are Arrhenius plots for catalysed and uncatalyzed decarboxylation reactions of methyl palmitate. The calculated activation energy drops from 36.89 kcal/mol for uncatalyzed reaction to 25.66, 19.34, 15.32, 14.40 and 11.69 kcal/mol for the α -NiMoO₄ (110), β -NiMoO₄(110), α -NiMoO₄ (021), β -NiMoO₄ (021), and Ni₃Mo catalysed reactions respectively. Being in the vicinity of the catalyst makes the O-CH₃ bond weaker hence making it easier to cleave which in turn lowers the activation energy. The presence of Ni₃Mo catalyst reduces the activation barrier the most when compared to NiMoO₄ and uncatalyzed reaction[334]. The 021 planes of NiMoO₄ appear to be catalytically performing better than 110 as shown by the lower activation energies. Compared to experimental results, the activation energies obtained in this study are slightly higher than the one reported on the decarboxylation methyl palmitate using NiMoK-TS1, which was 10.11 kcal/mol[125]. In the experiment, catalysts promoter and support were used, both of which improve catalyst performance, (Table 6. 1). The activation energy obtained from the uncatalyzed reaction is in the same range as the one obtained by Santos et al [324] in the experimental uncatalyzed pyrolysis of sunflower oil (Table 6. 1)

Table 6. 1: Summary of Activation energies calculated from this work and reported in literature.

CATALYST	$E_a(kcal/mol)$	REF
No catalyst	36.89	This work
Experimental uncatalyzed TG	37.04- 52.58	[324]
α -NiMoO ₄ (110)	25.65	This work
α -NiMoO ₄ (021)	15.32	This work
β -NiMoO ₄ (110)	19.34	This work
β -NiMoO ₄ (021)	14.40	This work
Ni ₃ Mo (101)	11.69	This work
NiMoK-TS1	10.11	[125]

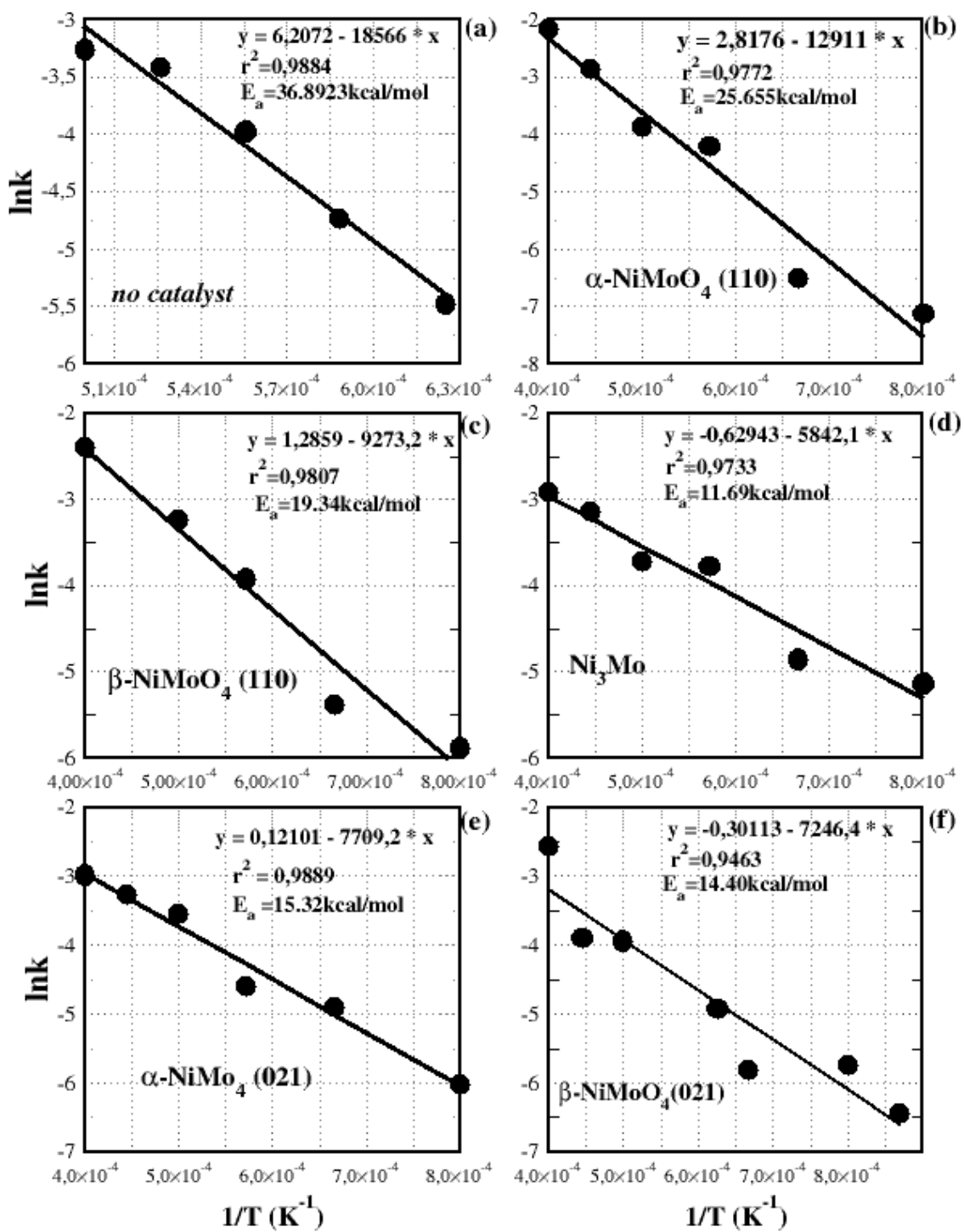


Figure 88: Arrhenius plots for the production of carbon dioxide (a) system with no catalyst. (b) $\alpha\text{-NiMoO}_4$ (110), (c) $\beta\text{-NiMoO}_4$ (110), (d) Ni_3Mo (101), (e) $\alpha\text{-NiMoO}_4$ (021), (f) $\beta\text{-NiMoO}_4$ (021).

6.4 Conclusions

Reactive force field molecular dynamics (ReaxFF-MD) was used to investigate the decarboxylation of methyl palmitate over the (021), (110) surfaces of α and β -NiMoO₄ and (101) plane of Ni₃Mo. The reliability of the method on studying the decarboxylation of MP was verified by comparing the bond dissociation enthalpies calculated using DFT (B3LYP/ 6-311 + g (d, p) to those from Vasenkov et al. derived parameters[189]. The results obtained showed a strong correlation between the two, showing the reliability of applying ReaxFF in this study. The results show that decarboxylation is initiated by the cleavage of O-CH₃ bond which results in the formation of CH₃[•] and C₁₆H₃₁O₂[•] radicals. The C₁₆H₃₁O₂[•] radical then undergoes decarboxylation to produce CO₂ and another radical C₁₅H₃₁[•]. The initial production channel of C₂H₄ which was observed in high quantities is from β -scission decomposition of the C₁₅H₃₁[•] radical. The introduction of catalyst reduces the temperature at which production of C₂H₄ begins. The amount of C₂H₄ is almost double in the presence of a catalyst. In the uncatalyzed and NiMoO₄ catalysed systems there was a gradual increase in the amount of C₂H₄ generated. However, in the Ni₃Mo catalysed system we observed a gradual increase in the amount of C₂H₄ produced until a maximum is reached, which was followed by a decrease as it fragmented to form C₂H₂ and H₂ gases. Similarly, the CO₂ was reduced to CO in the presence of Ni₃Mo catalyst, indicating that Ni₃Mo was more active than NiMoO₄. The increase in temperature also increases the rate of conversion of methyl palmitate and the amount of CO₂ and C₂H₄ formed. The yield of the experimentally observed major product of C₁₅H₃₀ ranged between 6-12% under simulation conditions at 2000K. An increase in temperature had a negative effect in the yield of long-chain hydrocarbons as it resulted in more cracking. The effect of support needs to be investigated in future to find out if it will help reduce this cracking. The results also show that the presence of a catalyst also reduces the activation energy of the reaction. The Ni₃Mo catalysed system had the lowest activation energy of 11.69 kcal/mol which is comparable to experimental results of 10.11kcal/mol[125]

CHAPTER 7

Conclusions and further work

In Chapter 4 of this thesis, the structural properties of the binary mixtures of cosolvents commonly used in transesterification reactions with triglycerides were investigated using molecular dynamics. In Chapter 5 the study was then expanded to ternary mixtures of triglycerides/methanol/cosolvents where thermodynamics properties were used to investigate the miscibility of methanol in triglycerides and the following conclusions were made:

Based on the findings presented in Chapter 4, it is concluded that changes in partial densities can be used as a physical indicator of miscibility. In systems where miscibility is observed, uniform partial density is noticed across the simulation box. Good cosolvents demonstrated strong interactions with both the polar and saturated parts of triolein. When dissolution or mixing occurs, a single triolein molecule is solvated by several cosolvent molecules. In terms of site-specific interactions, the strongest interactions of ether-based cosolvent molecules with both the polar and non-polar parts of FAMES are via carbon atoms connected to the ethereal oxygen. In the presence of solvents that dissolve it, triolein prefers to exist in the propeller conformation, but when there is less or no solvation, it prefers the trident conformation. THF was found to be the most miscible, followed by CPME, DEE, and hexane.

In Chapter 5, the Flory-Huggins theory of solutions was employed to investigate the thermodynamics of mixing in a ternary system comprising triolein, methanol, and cosolvents (tetrahydrofuran or diethyl ether). The binary interaction parameters between methanol and cosolvent remained relatively constant along the phase boundary. The Gibbs free energy of mixing showed the presence of both mixed and unmixed phases. The activities of components derived using the Flory-Huggins model were compared to those derived using the UNIFAC model, and both models showed good agreement in the region where UNIFAC predicts phase separation, $a_i > 1$ the Flory-Huggins derived activities are also greater than 1 showing a good agreement between two models.

The focus of Chapter 6 was to enhance the flow characteristics and oxidative stability of biodiesel by converting it into green diesel or hydrocarbons. ReaxFF-MD was used to investigate the decarboxylation of methyl palmitate over the (021), (110) planes of α -NiMoO₄ and β -NiMoO₄ and (101) plane of Ni₃Mo. The model predicts that both nickel molybdates and NiMo alloys are potentially active catalysts because the number of stable products, carbon dioxide, and ethene were higher than they were without the catalyst. The stronger adsorption of C₂H₄ and CO₂ onto Ni₃Mo than on molybdates is noted. This eventually leads to the production of CO and H₂. The catalyzed and uncatalyzed decomposition of methyl palmitate was found to follow first-order kinetics, from which the activation energies (E_a) were determined. The presence of a catalyst reduced the activation of the reaction from 36.89 kcal/mol in an uncatalyzed system to 25.66, 19.34, 15.32, 14.40, and 11.69 kcal/mol for the α -NiMoO₄ (110), β -NiMoO₄(110), α -NiMoO₄ (021), β -NiMoO₄ (021), and Ni₃Mo (101) catalyzed reactions, respectively.

7.1 Future Works

The results presented in Chapter 4, of this thesis are encouraging in such that we were able to know what structural properties we need to look for when looking for cosolvents for a system. The study focused on the interactions between cosolvents and triolein. Further investigation is still recommended on the dispersion of methanol in these solvents. This will provide a clear picture of all interactions that drive the miscibility of the cosolvent/triolein/methanol system.

Chapter 5 of the study investigated the effect of adding a cosolvent on the dispersion between methanol and triglycerides, using Flory Huggins's theory. To accurately simulate the experimental system, the simulated oil should be a mixture of different fatty acids with varying chain lengths and compositions, instead of a single type like triolein. It is recommended to theoretically reproduce the phase diagram since triolein alone cannot replicate the experimentally observed phase diagram. The stability of the phases should also be investigated since this study focused on miscibility and phase separation. The statistical method, UNIFAC was compared with our model, and it was found to agree. However, applying our model to experimentally calculated binary interactions will demonstrate its reliability and robustness.

The results presented in Chapter 6 demonstrated how binary Ni/Mo catalysed methyl palmitate decarboxylation. There is still a lot of work to be done to gain a better understanding of the system. The Vasenkov et al.[189], derived parameters were parameterized for high pressure, and

high-temperature conditions, and the applicability of the ReaxFF was performed using coal containing sulphur and nitrogen, which may have resulted in shortcomings in our study. It is necessary to reparametrize the systems using esters and catalysts used in this research. Supports are also used in experiments and have been shown to reduce hydrocarbon cracking. The effects of support should be studied further in the future to see if it can help reduce cracking under simulation conditions. In this study, we only looked at pristine surfaces, in the future, defects can be introduced in the catalyst surfaces and the results compared to those of pristine surfaces.

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APPENDIX A

Single Molecule Coordinates

A1 XYZ coordinates of Molecules used in Chapter 4

CPME

-1PME	H17	1	0.235	0.151	-0.049
-1PME	C6	2	0.169	0.085	0.009
-1PME	H16	3	0.182	0.110	0.115
-1PME	C5	4	0.198	-0.065	-0.015
-1PME	H14	5	0.272	-0.103	0.056
-1PME	H15	6	0.239	-0.081	-0.115
-1PME	C4	7	0.061	-0.137	-0.001
-1PME	H12	8	0.061	-0.214	0.078
-1PME	H13	9	0.033	-0.187	-0.095
-1PME	C3	10	-0.043	-0.027	0.027
-1PME	H11	11	-0.057	-0.015	0.136
-1PME	C7	12	0.021	0.101	-0.029
-1PME	H18	13	0.008	0.101	-0.139
-1PME	H19	14	-0.024	0.194	0.010
-1PME	O2	15	-0.168	-0.064	-0.031
-1PME	C1	16	-0.275	0.021	0.005
-1PME	H8	17	-0.263	0.123	-0.033
-1PME	H9	18	-0.366	-0.022	-0.038
-1PME	H10	19	-0.288	0.026	0.115
0.00000	0.00000	0.00000			

DIETHYL ETHER

00GQ0	H11	1	0.271	-0.102	0.019
00GQ0	C4	2	0.236	0.001	0.026
00GQ0	H8	3	0.307	0.066	-0.027
00GQ0	H9	4	0.235	0.030	0.132
00GQ0	C2	5	0.097	0.015	-0.035
00GQ0	H6	6	0.099	-0.012	-0.142
00GQ0	H7	7	0.063	0.119	-0.029
00GQ0	O1	8	0.009	-0.072	0.035
00GQ0	C1	9	-0.124	-0.074	-0.016
00GQ0	H1	10	-0.170	-0.165	0.025
00GQ0	H2	11	-0.123	-0.084	-0.125
00GQ0	C3	12	-0.207	0.048	0.025
00GQ0	H3	13	-0.311	0.036	-0.010
00GQ0	H4	14	-0.209	0.059	0.134
00GQ0	H5	15	-0.168	0.141	-0.019
0.00000	0.00000	0.00000			

Tetrahydrofuran

0THFN	H8	1	-0.109	-0.139	0.096
0THFN	C4	2	-0.071	-0.114	-0.004
0THFN	H7	3	-0.093	-0.197	-0.071
0THFN	O1	4	-0.138	0.002	-0.055
0THFN	C1	5	-0.070	0.114	0.002
0THFN	H1	6	-0.101	0.127	0.108
0THFN	H2	7	-0.099	0.203	-0.054
0THFN	C2	8	0.079	0.078	-0.007
0THFN	H3	9	0.138	0.126	0.072
0THFN	H4	10	0.120	0.111	-0.103
0THFN	C3	11	0.079	-0.077	0.002
0THFN	H5	12	0.125	-0.113	0.095
0THFN	H6	13	0.135	-0.121	-0.081
0.00000	0.00000	0.00000			

Hexane

0HEX2	H14	1	-0.408	-0.047	-0.000
0HEX2	C6	2	-0.322	0.022	-0.000
0HEX2	H12	3	-0.331	0.087	-0.088
0HEX2	H13	4	-0.331	0.086	0.089
0HEX2	C5	5	-0.190	-0.054	-0.000
0HEX2	H10	6	-0.185	-0.120	0.088
0HEX2	H11	7	-0.185	-0.120	-0.088
0HEX2	C4	8	-0.067	0.038	-0.000
0HEX2	H8	9	-0.071	0.104	0.088
0HEX2	H9	10	-0.071	0.104	-0.088
0HEX2	C3	11	0.067	-0.038	-0.000
0HEX2	H6	12	0.071	-0.104	0.088
0HEX2	H7	13	0.071	-0.104	-0.088
0HEX2	C2	14	0.190	0.054	-0.000
0HEX2	H4	15	0.185	0.120	0.088
0HEX2	H5	16	0.185	0.120	-0.088
0HEX2	C1	17	0.322	-0.022	-0.000
0HEX2	H1	18	0.331	-0.086	0.089
0HEX2	H2	19	0.408	0.047	-0.000
0HEX2	H3	20	0.331	-0.086	-0.089
0.00000	0.00000	0.00000			

GVL

0S44R	O6	1	-0.287	-0.084	-0.035
0S44R	C5	2	-0.177	-0.039	-0.010
0S44R	C4	3	-0.135	0.106	0.009
0S44R	H14	4	-0.167	0.137	0.110
0S44R	H15	5	-0.186	0.170	-0.063
0S44R	C3	6	0.018	0.101	-0.004
0S44R	H12	7	0.070	0.175	0.056
0S44R	H13	8	0.047	0.115	-0.109
0S44R	C2	9	0.051	-0.043	0.041
0S44R	O7	10	-0.069	-0.120	0.006
0S44R	H11	11	0.060	-0.048	0.150
0S44R	C1	12	0.171	-0.107	-0.026
0S44R	H8	13	0.261	-0.051	0.000
0S44R	H9	14	0.184	-0.210	0.008
0S44R	H10	15	0.160	-0.106	-0.135
0.00000	0.00000	0.00000			

Dioxane

0G256	H8	1	0.078	-0.123	-0.132
0G256	C4	2	0.073	-0.117	-0.022
0G256	H7	3	0.127	-0.203	0.020
0G256	C3	4	-0.073	-0.117	0.022
0G256	H5	5	-0.078	-0.123	0.132
0G256	H6	6	-0.127	-0.203	-0.020
0G256	O1	7	-0.140	0.000	-0.024
0G256	C2	8	-0.073	0.117	0.022
0G256	H3	9	-0.078	0.123	0.132
0G256	H4	10	-0.127	0.203	-0.020
0G256	C1	11	0.073	0.117	-0.022
0G256	O2	12	0.140	0.000	0.024
0G256	H1	13	0.078	0.123	-0.132
0G256	H2	14	0.127	0.203	0.020
0.00000	0.00000	0.00000			

Triolein

0TRIO	C57	1	0.031	1.641	0.165
0TRIO	C56	2	0.008	1.493	0.144
0TRIO	C51	3	-0.132	1.464	0.094
0TRIO	C50	4	-0.153	1.316	0.074
0TRIO	C49	5	-0.294	1.287	0.024
0TRIO	C48	6	-0.315	1.139	0.004
0TRIO	C47	7	-0.456	1.110	-0.044
0TRIO	C38	8	-0.480	0.961	-0.063

OTRIO	C37	9	-0.490	0.887	0.065
OTRIO	H103	10	-0.478	0.947	0.156
OTRIO	C36	11	-0.511	0.755	0.073
OTRIO	H102	12	-0.517	0.706	0.171
OTRIO	C35	13	-0.528	0.667	-0.045
OTRIO	C34	14	-0.527	0.520	-0.007
OTRIO	C33	15	-0.547	0.432	-0.129
OTRIO	C32	16	-0.541	0.286	-0.092
OTRIO	C31	17	-0.566	0.198	-0.213
OTRIO	C30	18	-0.554	0.051	-0.177
OTRIO	C29	19	-0.583	-0.036	-0.297
OTRIO	C6	20	-0.564	-0.181	-0.265
OTRIO	O6	21	-0.482	-0.260	-0.311
OTRIO	O3	22	-0.654	-0.227	-0.171
OTRIO	C3	23	-0.636	-0.362	-0.127
OTRIO	C2	24	-0.728	-0.379	-0.006
OTRIO	H3	25	-0.831	-0.341	-0.032
OTRIO	O2	26	-0.693	-0.293	0.103
OTRIO	C5	27	-0.570	-0.300	0.162
OTRIO	O5	28	-0.493	-0.390	0.131
OTRIO	C18	29	-0.549	-0.189	0.261
OTRIO	C19	30	-0.459	-0.081	0.204
OTRIO	C20	31	-0.315	-0.128	0.193
OTRIO	C21	32	-0.231	-0.029	0.115
OTRIO	C22	33	-0.089	-0.080	0.100
OTRIO	C23	34	-0.006	0.013	0.014
OTRIO	C24	35	0.135	-0.040	-0.003
OTRIO	C25	36	0.217	0.044	-0.093
OTRIO	H101	37	0.171	0.138	-0.127
OTRIO	C26	38	0.341	0.012	-0.132

0TRIO	H100	39	0.398	0.079	-0.198
0TRIO	C27	40	0.411	-0.112	-0.090
0TRIO	C28	41	0.545	-0.131	-0.158
0TRIO	C43	42	0.650	-0.035	-0.107
0TRIO	C44	43	0.781	-0.054	-0.179
0TRIO	C45	44	0.887	0.040	-0.125
0TRIO	C46	45	1.019	0.021	-0.197
0TRIO	C54	46	1.123	0.120	-0.148
0TRIO	C55	47	1.257	0.096	-0.212
0TRIO	C1	48	-0.740	-0.526	0.037
0TRIO	O1	49	-0.624	-0.598	-0.006
0TRIO	C4	50	-0.558	-0.675	0.085
0TRIO	O4	51	-0.609	-0.694	0.195
0TRIO	C7	52	-0.429	-0.729	0.031
0TRIO	C8	53	-0.312	-0.671	0.109
0TRIO	C9	54	-0.180	-0.709	0.045
0TRIO	C10	55	-0.064	-0.660	0.129
0TRIO	C11	56	0.068	-0.682	0.057
0TRIO	C12	57	0.185	-0.642	0.145
0TRIO	C13	58	0.316	-0.651	0.070
0TRIO	C14	59	0.432	-0.622	0.157
0TRIO	H104	60	0.414	-0.632	0.265
0TRIO	C15	61	0.553	-0.587	0.112
0TRIO	H99	62	0.635	-0.568	0.184
0TRIO	C16	63	0.588	-0.569	-0.031
0TRIO	C17	64	0.737	-0.573	-0.057
0TRIO	C39	65	0.807	-0.448	-0.010
0TRIO	C40	66	0.955	-0.453	-0.042
0TRIO	C41	67	1.028	-0.331	0.011
0TRIO	C42	68	1.174	-0.332	-0.029

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0TRIO C52 69 1.248 -0.213 0.029
0TRIO C53 70 1.393 -0.213 -0.013
0.00000 0.00000 0.00000

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A2 XYZ coordinates of the molecules used in CHAPTER 5, generated by LIGPARGEN

Triolein

```

1TRI C00 1 0.100 0.100 0.000
1TRI C01 2 -0.052 0.100 0.000
1TRI C02 3 -0.107 0.100 0.142
1TRI C03 4 -0.260 0.100 0.142
1TRI C04 5 -0.314 0.100 0.285
1TRI C05 6 -0.467 0.101 0.285
1TRI C06 7 -0.521 0.101 0.428
1TRI C07 8 -0.674 0.102 0.427
1TRI C08 9 -0.727 0.102 0.567
1TRI C09 10 -0.803 0.003 0.617
1TRI C0A 11 -0.856 0.003 0.757
1TRI C0B 12 -1.009 0.003 0.757
1TRI C0C 13 -1.064 0.004 0.899
1TRI C0D 14 -1.216 0.003 0.897
1TRI C0E 15 -1.272 0.004 1.040
1TRI C0F 16 -1.425 0.004 1.038
1TRI C0G 17 -1.482 0.004 1.179
1TRI C0H 18 -1.438 0.125 1.258
1TRI O0I 19 -1.376 0.120 1.363
1TRI O0J 20 -1.477 0.239 1.195
1TRI C0K 21 -1.447 0.361 1.266
1TRI C0M 22 -1.549 0.386 1.378
1TRI C0N 23 -1.518 0.519 1.447
1TRI O0O 24 -1.608 0.543 1.556
1TRI C0P 25 -1.578 0.477 1.671

```

1TRI	O0Q	26	-1.480	0.406	1.689
1TRI	C0R	27	-1.684	0.504	1.775
1TRI	C0S	28	-1.821	0.460	1.724
1TRI	C0T	29	-1.930	0.485	1.827
1TRI	C0U	30	-2.065	0.440	1.772
1TRI	C0V	31	-2.176	0.465	1.873
1TRI	C0W	32	-2.311	0.420	1.818
1TRI	C0X	33	-2.422	0.444	1.919
1TRI	C0Y	34	-2.554	0.400	1.864
1TRI	C0Z	35	-2.628	0.303	1.919
1TRI	C10	36	-2.760	0.258	1.865
1TRI	C11	37	-2.871	0.283	1.966
1TRI	C12	38	-3.006	0.238	1.911
1TRI	C13	39	-3.117	0.263	2.012
1TRI	C14	40	-3.252	0.217	1.956
1TRI	C15	41	-3.364	0.242	2.057
1TRI	C16	42	-3.498	0.197	2.002
1TRI	C17	43	-3.610	0.222	2.102
1TRI	O18	44	-1.679	0.395	1.314
1TRI	C19	45	-1.747	0.277	1.302
1TRI	O1A	46	-1.723	0.175	1.366
1TRI	C1B	47	-1.847	0.284	1.190
1TRI	C1C	48	-1.984	0.240	1.239
1TRI	C1D	49	-2.087	0.247	1.127
1TRI	C1E	50	-2.224	0.202	1.179
1TRI	C1F	51	-2.330	0.208	1.069
1TRI	C1G	52	-2.466	0.163	1.122
1TRI	C1H	53	-2.572	0.169	1.013
1TRI	C1I	54	-2.705	0.125	1.066
1TRI	C1J	55	-2.813	0.204	1.069

1TRI	C1K	56	-2.946	0.161	1.122
1TRI	C1M	57	-3.052	0.166	1.012
1TRI	C1N	58	-3.188	0.122	1.066
1TRI	C1O	59	-3.295	0.127	0.956
1TRI	C1P	60	-3.430	0.083	1.011
1TRI	C1Q	61	-3.537	0.088	0.901
1TRI	C1R	62	-3.673	0.044	0.955
1TRI	C1S	63	-3.779	0.049	0.846
1TRI	H1T	64	0.138	0.100	-0.103
1TRI	H1U	65	0.139	0.011	0.051
1TRI	H1V	66	0.139	0.189	0.051
1TRI	H1W	67	-0.088	0.012	-0.054
1TRI	H1X	68	-0.088	0.188	-0.054
1TRI	H1Y	69	-0.070	0.188	0.196
1TRI	H1Z	70	-0.070	0.012	0.196
1TRI	H20	71	-0.297	0.012	0.089
1TRI	H21	72	-0.296	0.189	0.089
1TRI	H22	73	-0.277	0.189	0.339
1TRI	H23	74	-0.277	0.012	0.339
1TRI	H24	75	-0.504	0.012	0.232
1TRI	H25	76	-0.504	0.189	0.232
1TRI	H26	77	-0.484	0.189	0.481
1TRI	H27	78	-0.484	0.013	0.482
1TRI	H28	79	-0.711	0.015	0.371
1TRI	H29	80	-0.711	0.191	0.376
1TRI	H2A	81	-0.701	0.188	0.629
1TRI	H2B	82	-0.829	-0.082	0.555
1TRI	H2C	83	-0.819	0.090	0.813
1TRI	H2D	84	-0.819	-0.086	0.809
1TRI	H2E	85	-1.046	-0.085	0.703

1TRI	H2F	86	-1.046	0.092	0.703
1TRI	H2G	87	-1.027	0.092	0.952
1TRI	H2H	88	-1.027	-0.085	0.953
1TRI	H2I	89	-1.253	-0.085	0.844
1TRI	H2J	90	-1.253	0.092	0.844
1TRI	H2K	91	-1.234	0.092	1.092
1TRI	H2M	92	-1.235	-0.084	1.094
1TRI	H2N	93	-1.461	-0.085	0.986
1TRI	H2O	94	-1.461	0.091	0.983
1TRI	H2P	95	-1.451	-0.086	1.234
1TRI	H2Q	96	-1.592	0.003	1.176
1TRI	H2R	97	-1.454	0.441	1.191
1TRI	H2S	98	-1.344	0.359	1.303
1TRI	H2T	99	-1.549	0.305	1.451
1TRI	H2U	100	-1.532	0.602	1.377
1TRI	H2V	101	-1.414	0.523	1.482
1TRI	H2W	102	-1.682	0.610	1.800
1TRI	H2X	103	-1.658	0.448	1.866
1TRI	H2Y	104	-1.817	0.353	1.699
1TRI	H2Z	105	-1.845	0.513	1.632
1TRI	H30	106	-1.934	0.592	1.852
1TRI	H31	107	-1.907	0.431	1.920
1TRI	H32	108	-2.061	0.333	1.748
1TRI	H33	109	-2.087	0.494	1.680
1TRI	H34	110	-2.180	0.572	1.898
1TRI	H35	111	-2.154	0.410	1.966
1TRI	H36	112	-2.306	0.313	1.792
1TRI	H37	113	-2.332	0.474	1.724
1TRI	H38	114	-2.428	0.551	1.942
1TRI	H39	115	-2.399	0.392	2.013

1TRI	H3A	116	-2.589	0.450	1.774
1TRI	H3B	117	-2.592	0.252	2.009
1TRI	H3C	118	-2.753	0.151	1.841
1TRI	H3D	119	-2.783	0.310	1.771
1TRI	H3E	120	-2.875	0.390	1.991
1TRI	H3F	121	-2.849	0.229	2.059
1TRI	H3G	122	-3.001	0.131	1.886
1TRI	H3H	123	-3.027	0.292	1.818
1TRI	H3I	124	-3.121	0.369	2.037
1TRI	H3J	125	-3.095	0.208	2.105
1TRI	H3K	126	-3.247	0.111	1.931
1TRI	H3M	127	-3.273	0.272	1.863
1TRI	H3N	128	-3.367	0.349	2.082
1TRI	H3O	129	-3.342	0.188	2.150
1TRI	H3P	130	-3.495	0.090	1.977
1TRI	H3Q	131	-3.521	0.251	1.909
1TRI	H3R	132	-3.592	0.166	2.195
1TRI	H3S	133	-3.706	0.189	2.061
1TRI	H3T	134	-3.617	0.328	2.127
1TRI	H3U	135	-1.811	0.219	1.110
1TRI	H3V	136	-1.851	0.386	1.151
1TRI	H3W	137	-2.015	0.304	1.322
1TRI	H3X	138	-1.979	0.138	1.278
1TRI	H3Y	139	-2.056	0.182	1.044
1TRI	H3Z	140	-2.094	0.349	1.088
1TRI	H40	141	-2.254	0.267	1.262
1TRI	H41	142	-2.217	0.100	1.218
1TRI	H42	143	-2.300	0.143	0.985
1TRI	H43	144	-2.337	0.310	1.030
1TRI	H44	145	-2.495	0.228	1.206

1TRI	H45	146	-2.458	0.061	1.162
1TRI	H46	147	-2.544	0.102	0.930
1TRI	H47	148	-2.578	0.270	0.972
1TRI	H48	149	-2.712	0.023	1.103
1TRI	H49	150	-2.806	0.306	1.032
1TRI	H4A	151	-2.974	0.227	1.204
1TRI	H4B	152	-2.941	0.059	1.163
1TRI	H4C	153	-3.023	0.101	0.928
1TRI	H4D	154	-3.060	0.268	0.972
1TRI	H4E	155	-3.218	0.187	1.149
1TRI	H4F	156	-3.180	0.020	1.105
1TRI	H4G	157	-3.265	0.062	0.873
1TRI	H4H	158	-3.302	0.229	0.917
1TRI	H4I	159	-3.460	0.148	1.094
1TRI	H4J	160	-3.423	-0.020	1.050
1TRI	H4K	161	-3.507	0.023	0.818
1TRI	H4M	162	-3.544	0.190	0.862
1TRI	H4N	163	-3.703	0.108	1.038
1TRI	H4O	164	-3.666	-0.059	0.994
1TRI	H4P	165	-3.790	0.151	0.807
1TRI	H4Q	166	-3.876	0.017	0.886
1TRI	H4R	167	-3.753	-0.017	0.763
1.00000	1.00000	1.00000			

Diethyl ether

1DEE	C00	1	0.100	0.100	0.000
1DEE	C01	2	-0.052	0.100	0.000
1DEE	O02	3	-0.097	0.100	0.135
1DEE	C03	4	-0.239	0.100	0.143
1DEE	C04	5	-0.279	0.100	0.290
1DEE	H05	6	0.139	0.100	-0.102
1DEE	H06	7	0.139	0.012	0.053
1DEE	H07	8	0.139	0.188	0.052
1DEE	H08	9	-0.089	0.011	-0.051
1DEE	H09	10	-0.089	0.189	-0.051
1DEE	H0A	11	-0.279	0.010	0.094
1DEE	H0B	12	-0.279	0.189	0.094
1DEE	H0C	13	-0.238	0.012	0.341
1DEE	H0D	14	-0.388	0.100	0.300
1DEE	H0E	15	-0.238	0.188	0.340
1.00000	1.00000	1.00000			

Methanol

1MET	C00	1	0.100	0.100	0.000
1MET	O01	2	-0.042	0.100	0.000
1MET	H02	3	0.136	0.100	-0.103
1MET	H03	4	0.136	0.012	0.053
1MET	H04	5	0.135	0.190	0.051
1MET	H05	6	-0.070	0.019	-0.046
1.00000	1.00000	1.00000			

THF

1THF	C00	1	0.100	0.100	0.000
1THF	C01	2	-0.051	0.100	0.000
1THF	C02	3	-0.082	0.100	0.148
1THF	O03	4	0.024	0.027	0.212
1THF	C04	5	0.131	0.011	0.119
1THF	H05	6	0.137	0.202	0.019
1THF	H06	7	0.144	0.064	-0.093
1THF	H07	8	-0.088	0.008	-0.046
1THF	H08	9	-0.095	0.185	-0.053
1THF	H09	10	-0.178	0.053	0.171
1THF	H0A	11	-0.082	0.202	0.189
1THF	H0B	12	0.134	-0.094	0.089
1THF	H0C	13	0.226	0.037	0.166
1.00000	1.00000	1.00000			

A3 coordinates of molecules used in CHAPTER 6

Ni₃Mo POSCAR

Ni6 Mo2

1.0

	4.2016816139	0.0000000000	0.0000000000
	0.0000000000	4.4277415276	0.0000000000
	0.0000000000	0.0000000000	4.9704699516
Ni	Mo		
6	2		
Cartesian			
	2.100840807	0.705457918	3.735176680
	0.0000000000	3.722283675	3.720528247
	2.100840807	2.950167490	0.0000000000
	0.0000000000	1.477573905	2.485234976
	0.0000000000	3.722283675	1.249941704
	2.100840807	0.705457918	1.235293272
	2.100840807	2.897700867	2.485234976
	0.0000000000	1.530040661	0.0000000000

α -NiMoO₄ POSCAR

9.5480327606	0.0000000000	0.0000000000
0.0000000000	8.7385540009	0.0000000000
-3.0989634771	0.0000000000	6.9685654340

Ni Mo O

8 8 32

Cartesian

7.289122754	4.369277000	1.093005645
-0.840053470	4.369277000	5.875559789
-1.549481739	2.746333769	3.484282717
-1.549481739	5.992220232	3.484282717
2.515106374	0.000000000	1.093005645
3.933962910	0.000000000	5.875559789
3.224534642	7.115610769	3.484282717
3.224534642	1.622943231	3.484282717
5.470055094	4.369277000	4.442140139
0.979014474	4.369277000	2.526425295
0.000000000	2.450672140	0.000000000

0.000000000	6.287881861	0.000000000
0.696038429	0.000000000	4.442140139
5.753030569	0.000000000	2.526425295
4.774016380	6.819949141	0.000000000
4.774016380	1.918604730	0.000000000
-0.734152409	5.693128751	1.657074720
7.183221423	5.693128751	5.311490818
7.183221423	3.045425250	5.311490818
-0.734152409	3.045425250	1.657074720
1.247444154	1.401036195	0.555663147
5.201625222	1.401036195	6.412902080
5.201625222	7.337517806	6.412902080
1.247444154	7.337517806	0.555663147
4.510992603	5.735623505	4.021035613
1.938076681	5.735623505	2.947529821
1.938076681	3.002930496	2.947529821
4.510992603	3.002930496	4.021035613
6.757486539	4.369277000	3.051300381
-0.308417020	4.369277000	3.917264846
5.256478337	4.369277000	6.352509316
1.192590854	4.369277000	0.616056326
4.039864194	1.323851880	1.657074720
2.409205328	1.323851880	5.311490818
2.409205328	7.414702251	5.311490818
4.039864194	7.414702251	1.657074720
6.021460534	5.770313195	0.555663147
0.427608842	5.770313195	6.412902080
0.427608842	2.968240806	6.412902080
6.021460534	2.968240806	0.555663147
-0.263023777	1.366346504	4.021035613

6.712093061	1.366346504	2.947529821
6.712093061	7.372207497	2.947529821
-0.263023777	7.372207497	4.021035613
1.983470158	0.000000000	3.051300381
4.465599218	0.000000000	3.917264846
0.482461957	0.000000000	6.352509316
5.966607234	0.000000000	0.616056326

β -NiMoO₄ POSCAR

1.0

10.1300001144	0.0000000000	0.0000000000
0.0000000000	9.2799997330	0.0000000000
-2.0758701485	0.0000000000	6.7060541944

O Ni Mo

32 8 8

Cartesian

-0.221281383	1.433759891	2.076194349
8.275411462	7.846239703	4.629859845
8.275411462	1.433759891	4.629859845
-0.221281383	7.846239703	2.076194349
4.843718561	6.073759896	2.076194349
3.210411405	3.206239837	4.629859845
3.210411405	6.073759896	4.629859845
4.843718561	3.206239837	2.076194349
1.309923724	3.244287788	0.202522842
6.744206098	6.035712221	6.503531327
6.744206098	3.244287788	6.503531327
1.309923724	6.035712221	0.202522842
6.374923933	7.884287378	0.202522842
1.679206041	1.395712078	6.503531327
1.679206041	7.884287378	6.503531327

6.374923933	1.395712078	0.202522842
2.865084627	1.347455954	2.626761425
5.189045401	7.932543641	4.079292570
5.189045401	1.347455954	4.079292570
2.865084627	7.932543641	2.626761425
7.930084684	5.987455959	2.626761425
0.124045344	3.292543774	4.079292570
0.124045344	5.987455959	4.079292570
7.930084684	3.292543774	2.626761425
1.355599684	0.000000000	0.244770974
6.698530538	0.000000000	6.461283370
6.420599439	4.639999866	0.244770974
1.633530178	4.639999866	6.461283370
0.699003535	0.000000000	4.381735837
7.355126582	0.000000000	2.324318358
5.764003441	4.639999866	4.381735837
2.290126525	4.639999866	2.324318358
1.323396513	0.000000000	2.422897324
6.730733754	0.000000000	4.283156870
6.388396269	4.639999866	2.422897324
1.665733395	4.639999866	4.283156870
0.000000000	1.698147148	0.000000000
0.000000000	7.581852447	0.000000000
5.065000057	6.338147153	0.000000000
5.065000057	2.941852580	0.000000000
7.190681724	0.000000000	0.637142192
0.863448211	0.000000000	6.068912102
2.125681667	4.639999866	0.637142192
5.928448268	4.639999866	6.068912102
-1.037935074	2.334847908	3.353027097

-1.037935074	6.945151549	3.353027097
4.027064983	6.974848051	3.353027097
4.027064983	2.305151959	3.353027097

Methyl Palmitate (XYZ)

C	1.491994	-0.384120	1.119725
C	2.137450	-0.453266	-0.267690
C	3.407924	0.397157	-0.388052
C	4.058730	0.339170	-1.775003
C	5.336528	1.178950	-1.891616
C	5.975523	1.132344	-3.284703
C	7.272774	1.942167	-3.396217
C	7.892068	1.915968	-4.798759
C	9.221620	2.672554	-4.900725
C	9.819282	2.674553	-6.312827
C	11.184875	3.365570	-6.401802
C	11.767854	3.395550	-7.819522
C	13.165338	4.021437	-7.890326
C	13.736075	4.072916	-9.312738
C	15.149199	4.658340	-9.384173
C	16.211631	3.736530	-8.818239
O	16.079133	2.558820	-8.593081
O	17.369191	4.403708	-8.613829
C	18.466731	3.612343	-8.122809
H	2.181357	-0.735442	1.894312
H	0.590107	-1.000641	1.173444
H	1.207795	0.642473	1.372827
H	2.377834	-1.496504	-0.507291
H	1.412671	-0.127925	-1.024276
H	4.134340	0.069156	0.367329
H	3.167730	1.440467	-0.143660

H	4.289731	-0.705256	-2.022790
H	3.334179	0.675773	-2.528207
H	6.065676	0.833188	-1.147096
H	5.109966	2.221487	-1.632154
H	6.179464	0.087661	-3.554207
H	5.253310	1.500247	-4.025391
H	8.002032	1.557443	-2.671153
H	7.077589	2.983012	-3.106178
H	8.047970	0.873278	-5.105545
H	7.177065	2.338696	-5.516839
H	9.943495	2.227832	-4.203126
H	9.077500	3.708822	-4.567443
H	9.917339	1.639405	-6.665457
H	9.117779	3.163850	-7.001380
H	11.890334	2.855368	-5.733072
H	11.098186	4.393115	-6.024321
H	11.085372	3.946443	-8.480408
H	11.814366	2.372295	-8.213752
H	13.129855	5.038952	-7.478004
H	13.845302	3.447292	-7.251400
H	13.076544	4.674266	-9.948616
H	13.752591	3.063415	-9.734869
H	15.216690	5.620551	-8.867166
H	15.434233	4.858236	-10.424119
H	19.296337	4.306171	-8.003964
H	18.722655	2.827101	-8.836639
H	18.210437	3.151604	-7.167272

APPENDIX A2

Gromacs commands

Construction of an initial configuration

```
gmx insert-molecules -ci TRI.gro -nmol 26 -box 6.6 6.6 6.6 -o h_box.gro
```

```
gmx insert-molecules -ci THF.gro -nmol 441 -f h_box.gro -o box_2.gro.
```

```
gmx insert-molecules -ci MET.gro -nmol 1448 -f box_2.gro -o triolein_thf_met.gro
```

Run commands.

Energy minimisation

```
gmx grompp -f minim.mdp -c gbl400_eth_600.gro -p gbl_eth.top -o em.tpr -maxwarn 3
```

```
gmx mdrun -v -deffnm em
```

NVT equilibration

```
gmx grompp -f nvt.mdp -c em.gro -p gbl_eth.top -o nvt.tpr -maxwarn 3
```

```
gmx mdrun -v -deffnm nvt
```

Production run

```
gmx grompp -f npt.mdp -c nvt.gro -t nvt.cpt -p gbl_eth.top -o npt.tpr -maxwarn 3
```

```
gmx mdrun -v -deffnm npt
```

Analysis

Calculation of the energy of the system

```
gmx energy -f npt.edr -b 100
```

(-b) means begin at and (-e) end

Calculation of the heat capacities

```
gmx energy -f npt.edr -b 5000 -fluct_props -nmol 1000
```

Calculation of the density of the system

```
gmx energy -f DENSITY.edr -s DENSITY.tpr
```

Calculation of the partial density

```
gmx density -s npt.tpr -f npt.xtc -d z -o density0.xvg -ng 2 -b 15000 -e 20000
```

Gromacs Molecular Dynamics Parameters (mdp files)

Energy minimization

; ions.mdp - used as input into grompp to generate ions.tpr

; Parameters describing what to do, when to stop and what to save

integrator = steep; Algorithm (steep = steepest descent minimization)

emtol = 100.0 ; Stop minimization when the maximum force < 1000.0 kJ/mol/nm

emstep = 0.01 ; Energy step size

nsteps = 5000; Maximum number of (minimization) steps to perform; Parameters describing how to find the neighbors of each atom and how to calculate the interactions

nstlist = 1; Frequency to update the neighbor list and long range forces

cutoff-scheme = Verlet

ns_type = grid; Method to determine neighbor list (simple, grid)

coulombtype = PME ; Treatment of long range electrostatic interactions

rcoulomb = 1.2 ; Short-range electrostatic cut-off

rvdw = 1.2 ; Short-range Van der Waals cut-off

pbcs = xyz ; Periodic Boundary Conditions (yes/no)

NVT equilibration

; Run parameters

integrator = md ; leap-frog integrator

nsteps = 100000 ; 2 * 50000 = 100 ps

dt = 0.001 ; 2 fs

; Output control

nstxout = 0 ; save coordinates every 0.0 ps

nstvout = 0 ; save velocities every 0.0 ps

nstfout = 0 ; save forces every 0.0 ps

nstenergy = 500 ; save energies every 1.0 ps

nstlog = 500 ; update log file every 1.0 ps

nstxout-compressed = 500; Bond parameters

continuation = no ; first dynamics run

```

constraint_algorithm = lincs          ; holonomic constraints
constraints          = none ; all bonds (even heavy atom-H bonds) constrained
lincs_iter           = 1              ; accuracy of LINCS
lincs_order          = 4              ; also related to accuracy; Neighborsearching
cutoff-scheme        = Verlet
ns_type              = grid           ; search neighboring grid cells
nstlist              = 10             ; 20 fs, largely irrelevant with Verlet
rcoulomb             = 1.2            ; short-range electrostatic cutoff (in nm)
rvdw                 = 1.2            ; short-range van der Waals cutoff (in nm); Electrostatics
coulombtype          = PME            ; Particle Mesh Ewald for long-range electrostatics
pme_order            = 4              ; cubic interpolationfourierspacing = 0.16 ; grid spacing for FFT
; Temperature coupling is on
tcoupl               = V-rescale       ; modified Berendsen thermostat
tc-grps              = System          ; two coupling groups - more accurate
tau_t                = 0.1            ; time constant, in ps
ref_t                = 298.15          ; reference temperature, one for each group, in K; Pressure
coupling is off
pcoupl               = no             ; no pressure coupling in NVT; Periodic boundary conditions
pbc                  = xyz            ; 3-D PBC; Dispersion correction
DispCorr             = EnerPres       ; account for cut-off vdW scheme; Velocity generation
gen_vel              = no             ; assign velocities from Maxwell distribution
gen_temp             = 298.15         ; temperature for Maxwell distribution
gen_seed             = -1             ; generate a random seed
Production run
; Run parameters
integrator           = md             ; leap-frog integrator
nsteps               = 20000000        ; 1 * 10000000 = 1000 ps
dt                   = 0.001           ; 1 fs
; Output control

```

```

nstxout      = 0           ; save coordinates every 0.0 ps
nstvout      = 0           ; save velocities every 0.0 ps
nstfout      = 0           ; save forccs every 0.0 ps
nstenergy    = 1000        ; save energies every 1.0 ps
nstlog       = 1000        ; update log file every 1.0 ps
nstxout-compressed = 500

; Bond parameters
continuation  = yes        ; Restarting after NVT
constraint_algorithm = lincs ; holonomic constraints
constraints   = hbonds     ; all bonds (even heavy atom-H bonds) constrained
lincs_iter    = 1          ; accuracy of LINCS
lincs_order   = 4          ; also related to accuracy

; Neighborsearching
cutoff-scheme = Verlet
ns_type       = grid       ; search neighboring grid cells
nstlist       = 10         ; 20 fs, largely irrelevant with Verlet scheme
rcoulomb      = 1.2         ; short-range electrostatic cutoff (in nm)
rvdw         = 1.2         ; short-range van der Waals cutoff (in nm)

; Electrostatics
coulombtype   = PME        ; Particle Mesh Ewald for long-range electrostatics
pme_order     = 4          ; cubic interpolation
fourierspacing = 0.16      ; grid spacing for FFT

; Temperature coupling is on
tcoupl       = V-rescale    ; modified Berendsen thermostat
tc-grps      = System      ; two coupling groups - more accurate
tau_t        = 0.1         ; time constant, in ps
ref_t        = 298.15      ; reference temperature, one for each group, in K

; Pressure coupling is on

```

```

pcoupl          = Parrinello-Rahman      ; Pressure coupling on in NPT
pcoupltype      = isotropic              ; uniform scaling of box vectors
tau_p           = 2.0                    ; time constant, in ps
ref_p           = 1.0                    ; reference pressure, in bar
compressibility = 4.5e-5                  ; isothermal compressibility of water, bar^-1
refcoord_scaling = com
; Periodic boundary conditions
pbc             = xyz                     ; 3-D PBC
; Dispersion correction
DispCorr        = EnerPres               ; account for cut-off vdW scheme
; Velocity generation
gen_vel         = no                      ; Velocity generation is off

```

Appendix A3

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