

Metathesis of biodiesel with Grubbs catalysts

G. Nel, P. van der Gryp, S. Marx. H.C.M. Vosloo
North-West University,

Focus area: Energy systems, Associate chair: Bioduels and other clean alternative fuels.
Catalyst Research Beneficiation (CRB)

Centre for Renewable and Sustainable Energy Studies

Abstract

Fossil fuels are limited and the increase in global demand for fossil fuels opens new areas of research for chemists and engineers alike. In recent years biomass sources has become an attractive alternative feedstock for the production of several intermediates and products. Biomass in the form of plant oils and animal fats contain triglycerides that can easily be converted to fatty acid esters also commonly known as biodiesel. The fatty acid esters that are produced vary considerably but studies have shown that the most common unsaturated fatty ester is oleic acid that is converted into methyl oleate in the biodiesel process. The double bond of the fatty acid ester is ideal for use with metathesis reactions like self- and cross-metathesis. The reactions of the fatty acid esters produce simple alkenes, mono- and diesters. The products that form are quite difficult to synthesize from other sources, making unsaturated fatty acid esters quite a valuable source. The metathesis of the unsaturated fatty acid esters found in biodiesel to intermediates for several. An investigation into the viability of metathesis as a method of extracting chemicals from the biodiesel was done.

Keywords: Metathesis, Methyl Oleate, Microwave, Biodiesel.

1. Introduction

1.1. Background

Society in modern times is very dependent on fossil fuels as a source of energy and chemicals for various industries. The transportation sector and electrical generation sector of countries is responsible for the consumption of almost 90% of all fossil fuels with the remaining 10% being utilised as a feedstock in the preparation of a wide variety of chemical products (Carlsson, 2009). Coal is the fossil fuel that is implemented and used throughout South Africa and it is used by several sectors, including SASOL (coal-to-liquid), ESKOM (electricity) and several of the mining sectors (Eberhard, 2011). Coal as a source of energy has several drawbacks, like not being renewable and adding to the increase in carbon dioxide levels. Energy usage also increases yearly by an alarming rate, which in turn places considerable strain on the dwindling feedstocks (Sanchez & Cardon, 2008).

The dependency of countries on fossil fuels needs to be reduced and a cleaner more sustainable alternative needs to be researched and implemented (Sanchez & Cardon, 2008). Hydro, solar, wind and nuclear energy are all renewable sources of energy that can be used to produce electricity but not as a transportation fuel or for the production of chemicals. Biomass from several sources like plant and animal wastes and products can be used to produce several different products (Huber & Dumesic, 2006). Biomass is mostly produced from crop-based feedstocks and is advantageous because they are renewable, products that form are biodegradable and the products that are produced has lower greenhouse and harmful gas emissions (Marvey, 2009).

Liquid fuels in the form of biodiesel are produced from a wide variety of sources, which include animal fats and plant oils, by the process known as transesterification (Knothe, 2007). The biodiesel is composed of several different carbon chain methyl esters varying in lengths of as short as C4 (Methyl butyrate) to as long as C20 (Methyl eicosenate). The most common methyl esters found in biodiesel is however in the C16 to C18 range (Balat & Balat, 2010). The C16 to C18 range include saturated and unsaturated esters.

It has also been shown that the composition of the oil has an effect on the quality of the biodiesel and changing the diesel composition can change the quality of the biodiesel positively or negatively (Knothe, 2008). The use of metathesis reactions can thus be used to change some of the biodiesel properties as well as for the production of chemicals for a wide variety of industries.

The most common catalyst that is used for metathesis is catalysts that are based on the second-generation Grubbs catalyst, like the second-generation Hoveyda-Grubbs catalyst. These catalysts show a high tolerability towards a wide variety of functional groups as well as high activity, making them ideal for use in the metathesis of methyl esters (Marvey, 2008).

The metathesis reaction of methyl esters produces several different products that can be grouped into three groups, namely, alkenes, mono- and diesters. The most common method of providing heat for the metathesis reaction is the use of a reflux column, to reduce loss of product and a heat source. This method however takes up to 48 hours for complete conversion to occur and methods of reducing the reaction time has been suggested, like using microwave irradiation as a heat source (Coquerel & Rodriguez, 2008). The implementation of microwave irradiation as a complementary activation method for olefin metathesis is therefore beneficial and should be investigated. The benefits of microwave irradiation include, lower catalyst loads, a dramatic decrease in reaction time as well as the change of allowing otherwise unproductive metathesis reactions to occur. When comparing the energy usage, Boddaert *et al.*, (2009) also found that microwave assisted irradiation uses less energy when compared to more classical methods of heating.

1.2. Objectives

The results of this investigation will contribute to the field of biodiesel as a method of extracting chemicals from the biodiesel and in the process changing the composition of the biodiesel. The results will show the viability of second-generation Grubbs catalyst for use in a biodiesel environment. The investigation is two-fold, two methods of heating will be compared and the following points act as a guideline for this investigation.

- Investigate the effect that temperature and reaction time has for the metathesis of methyl oleate using **Gr2** and a conventional method of heating
- Investigate the use of microwave irradiation as a heat source for the metathesis of methyl oleate using **Gr2** compared to that of conventional heating

2. Research methodology

2.1. Catalyst used

The catalyst that was used for this investigation is well known in the metathesis industry, has high activity and has a high tolerance towards several functional groups. Figure 1 depicts the second-generation Grubbs catalyst that was used in this study. The catalyst was obtained from Sigma-Aldrich and was used as is.

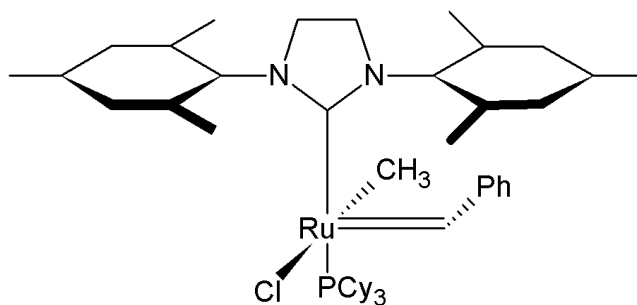


Figure 1: Second generation Grubbs catalyst (Gr2)

2.2. Chemicals used

Methyl oleate (99%), purchased from Sigma-Aldrich, was used as the substrate for the cross- and self-metathesis reaction. Methyl oleate is the most common unsaturated methyl ester that is present in biodiesel and will be used as a pure alternative to biodiesel. For GC analysis, n-dodecane(99%) from Sigma-Aldrich, *tert*-Butyl hydroperoxide 5.0-6.0M solution in decane (<4% H₂O) from Sigma-Aldrich and Dichloromethane (99%) from Merck was used. All chemicals were used as is, without further purification.

2.3. Experimental setup

A scientific series 2000 oven was used for the conventional method of heating and a normal kitchen microwave from LG was used for the microwave irradiation experiments. Reactions were conducted on small scale and to ensure a closed environment, standard 2 mL GC sample vials were used with septa. A bevel tip syringe, 50 μ L, was used to extract the reacted sample from the reaction vessel. The septa allows for a closed environment while allowing easy removal of the sample.

A constant amount of catalyst was used, 1:500 molar ratio of the methyl oleate, for all the reactions with 1.5 mL substrate. A standard solution was made, containing n-dodecane as an internal standard and the quench medium to deactivate the reaction. The sample that was removed with the syringe was added to the standard solution and analyzed in a GC-MS.

2.4. Analytical method

An Agilent 6890 gas chromatograph (GC) equipped with an Agilent 7683 Auto-injector was used to analyse the samples. The GC had a capillary HP-5MSUI (30m \times 320 μ m \times 0.25 μ m) column with a flame ionization detector (FID) and mass spectrometer was used for analysis. A split/splitless front inlet was used with an injection volume of 0.2 μ L and a ratio of 50:1. The inlet temperature was 250 $^{\circ}$ C at 13.6 kPa with a carrier gas Helium and the flow 79.3 mL/min. The oven was programmed to the following: Initial temperature of 50 $^{\circ}$ C with a residence time of 1 min. The temperature was then increased by 15 $^{\circ}$ C/min until the temperature reached 200 $^{\circ}$ C and was held at 200 $^{\circ}$ C for 1 minute. A rate of 7 $^{\circ}$ C/min was then used to heat until 290 $^{\circ}$ C where it was held for 15min. An external standard method was used to determine the distribution of the products after the metathesis reaction.

3. Results

All reactions were evaluated by grouping the multitude of products into three categories. Three types of products are formed during the metathesis reaction of methyl oleate, n-

alkenes, mono- and diesters. Grouping these products allows for a better evaluation of selectivity and yield.

3.1. Reactions using conventional heating

To determine the time it takes for the reaction to complete, a reaction was carried out at 50°C with 1:500 molar ratio (**Gr2**) catalyst added. Samples were taken every 20 minutes to generate data that can be used to determine the time it takes for the reaction to complete. To ensure complete conversion occurs, a reaction time of 360 minutes (6 hours) was used. The reaction was evaluated based upon the yield of the different product groups. Figure 1 illustrates the results of the metathesis reaction of methyl oleate.

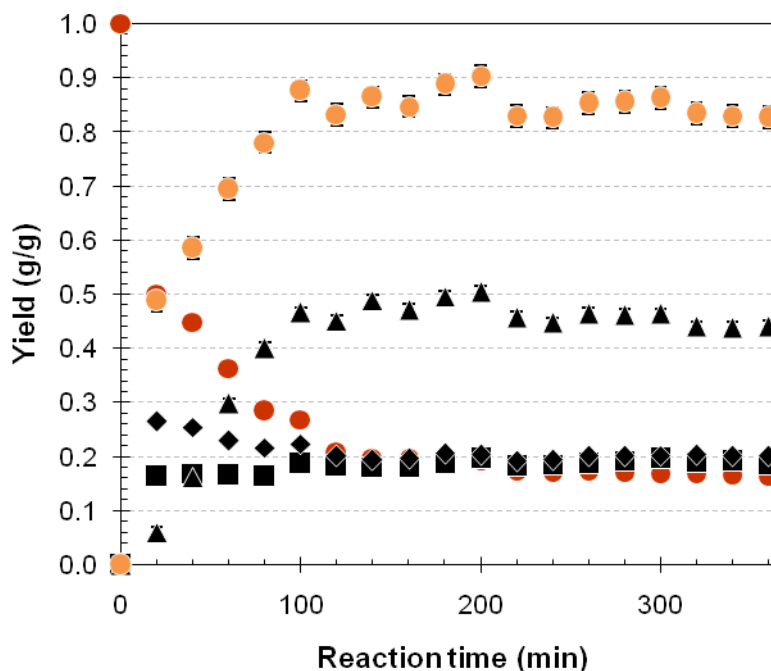


Figure 1: Product yield as a result of the metathesis of methyl oleate in the presence of Gr2 at 50°C, a molar catalyst ratio of 1:500 for 360 minutes.
[●Methyl oleate,■n-Alkenes,▲Monoesters,◆Diesters and ●Total metathesis]

The reaction starts to reach equilibrium after only 100 minutes but completely stabilises after 300 minutes of reaction time. Similar product distribution has been observed by Marvey *et al.* (2004) on a similar substrate and catalyst combination. The reaction was done to determine the reaction time required for the reaction to reach equilibrium, a reaction time of 300 minutes was chosen for further studies.

One of the biggest contributors to chemical reactions is reaction temperature. Reaction temperature influences the rate of the reaction, conversion over time as well as the effectivity of the catalyst at different temperatures. The time it takes for the reaction to complete has been determined and will be used to evaluate different reaction temperatures. Reactions were done at varying temperatures (30, 50, 70 and 90°C) with a molar catalyst ratio of 1:500 (**Gr2**). Figure 2 illustrates the effect that temperature has on the yield of the products.

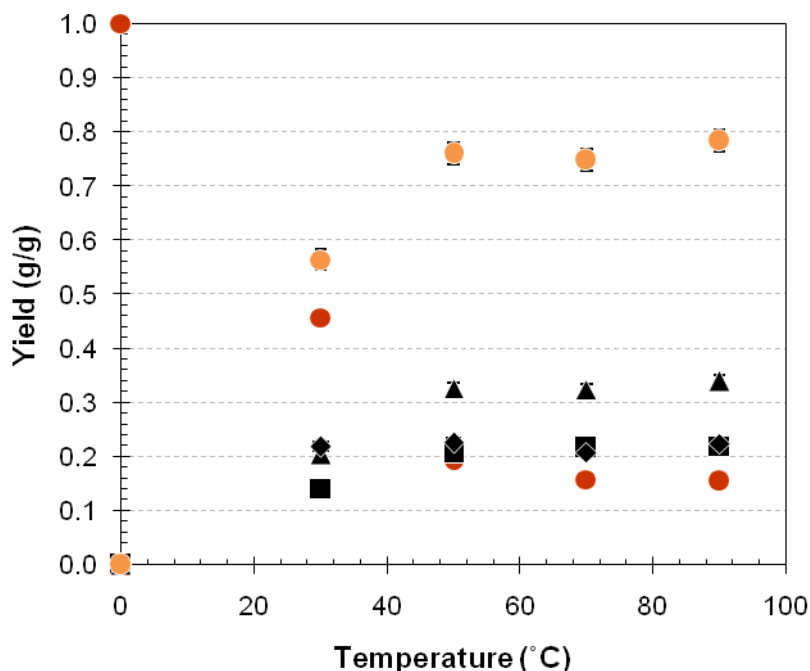


Figure 2: Product yield as a result of the metathesis of methyl oleate in the presence of Gr2 at varying temperatures and a molar catalyst ratio of 1:500 for 300 minutes.

[● Methyl oleate, ■ n-Alkenes, ▲ Monoesters, ◆ Diesters and ● Total metathesis]

From the results, it can be concluded that as temperature increases substrate usage increases as illustrated by the amount of methyl oleate consumed. The total metathesis product also increases as reaction temperature is increased. The difference between 70°C and 90°C is very small and falls within the experimental error of the reactions. It can be concluded that the temperature of the reaction influences the amount of product formed and that reaction should be done at temperatures above 70°C to ensure that the highest conversion is achieved.

3.2. Reactions using microwave irradiation

Since this is a comparative study on the difference between microwave irradiation and conventional methods of heating, the reaction time is again important. Reactions were done using 1:500 molar catalyst ratio (**Gr2**) at 900W for 15 minutes (900 seconds). The reaction was evaluated based on the yield of the different products and the usage of the substrate. Figure 3 illustrates the results of this reaction at different reaction times.

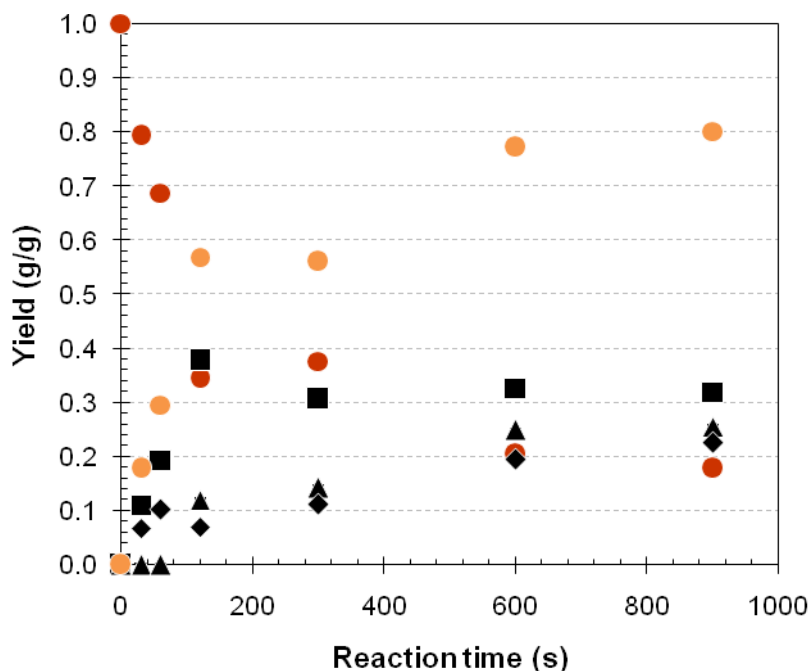


Figure 3: Product yield as a result of the metathesis of methyl oleate in the presence of Gr2 at 900 Watts and a molar catalyst ratio of 1:500.
 [●Methyl oleate,■n-Alkenes,▲Monoesters,◆Diesters and ●Total metathesis]

From the experiments, it can be concluded that reaction time has a significant impact on the product forming. The reaction starts to stabilise after only 600 seconds of reaction. The difference between 600 seconds and 900 seconds is very small with a slightly higher usage of substrate observed after 900 seconds of reaction. For the next set of experiments, 900 seconds of reaction time will be used, since it shows the highest conversion of methyl oleate.

The time it takes for the reaction to complete has been determined and the next step is to determine the effect that the amount of energy added has on the reaction. The reaction was done at different energies (180, 300, 450, 600 and 900W) for 900 seconds of reaction time. A molar catalyst ratio of 1:500 (Gr2) was used with the methyl oleate. The effect that different energy input has on the metathesis reaction of methyl oleate using microwave irradiation is illustrated by Figure 4.

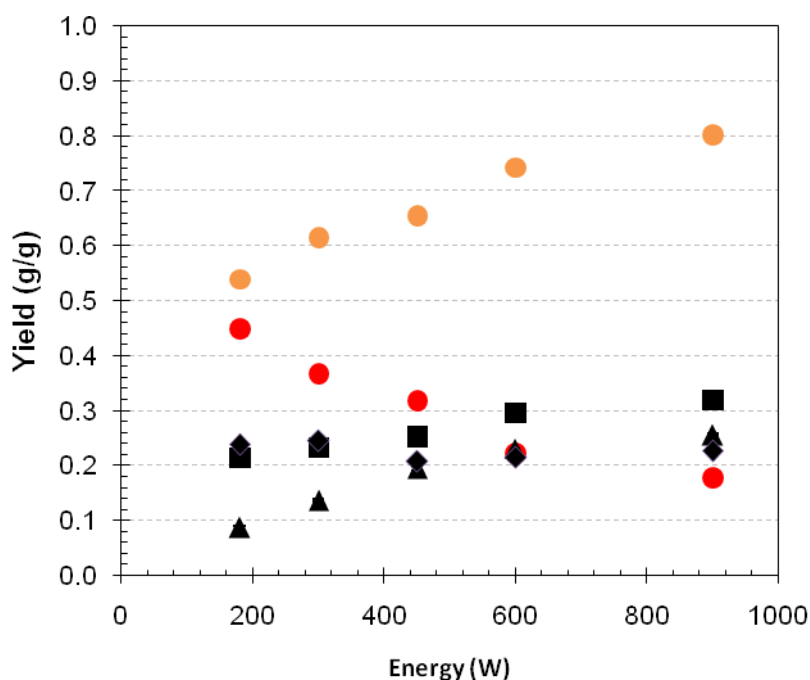


Figure 4: Product yield as a result of the metathesis of methyl oleate in the presence of Gr2 after 900 seconds at different energies and a molar catalyst ratio of 1:500.

[● Methyl oleate, ■ n-Alkenes, ▲ Monoesters, ◆ Diesters and ● Total metathesis]

The amount of energy provided by the irradiation has an effect on the yield of the product. The more energy added to the reaction, the higher the total metathesis yield and the higher the product usage. The highest yield is observed at the highest input energy of 900W.

To conclude the study the two methods of heating will be compared at the reaction conditions that resulted in the highest metathesis yield. The two methods will be evaluated on the reaction yield as well as energy required for the highest metathesis product yield. The comparative data is summarised in Table 1.

Table 1: Comparison of heating methods

Heating method	Conventional	Microwave
Catalyst	Gr2	Gr2
Reaction time (min)	300	15
Reaction conditions	90°C	900W
Methyl oleate (g/g)	0.154	0.178
n-Alkenes (g/g)	0.220	0.320
Monoesters (g/g)	0.341	0.256
Diesters (g/g)	0.224	0.226
Total yield (g/g)	0.785	0.802
Energy (W)	230	900
Energy (kJ)	4140	810

The biggest difference between the two methods is the time it takes for the reaction to complete. The conventional method of heating takes 20 times longer to achieve the same

amount of metathesis product. This alone, from a design point of view makes microwave irradiation superior. The size of a reaction vessel is determined by the flow through the reactor and the time it takes for the reaction to complete. Assuming that the flow stays constant, the only factor affecting the size of the reactor is the time it takes the reaction to complete.

The second way to compare the two methods is based on the yield of the products and usage of substrate. The two methods quite comparable and the small difference between the two cannot be used to make a conclusion solely based on the product formation.

Another important aspect of any heating method is the amount of energy that is used for the reaction to occur. The conventional method has a lower energy usage, but as soon as the reaction time is taken into account, the amount of energy required to do a reaction is 5 times higher, which makes a large difference.

4. Conclusions and recommendations

The second-generation Grubbs catalyst is a good catalyst for use in the biodiesel environment and metathesis reactions. The metathesis of a biodiesel component, methyl oleate, showed promising results, since it produced a variety of products, like n-alkenes, mono- and diesters.

As a method of heating, microwave irradiation was found to be the best. It had a considerable shorter reaction time as well as much smaller energy requirements to attain the same results as was found for the conventional method of heating. The yield of the two methods is also very comparable, with little to no difference.

Further studies can be used to improve this area of research, by increasing sample size, varying the catalyst load as well as using biodiesel from several different sources of oil, like soya, sunflower, etc.

References

- BALAT, M. & BALAT, H. 2010. Progress in biodiesel processing. *Applied energy*, 87:1815-1835.
- BODDAERT, T., COQUEREL, Y. & RODRIQUEZ, J. Microwave-assisted cross-metathesis of acrylonitrile. *Comptes Rendus Chimie*, 12:872-875.
- CALSSON, A.S. 009. Plant oils as feedstock alternatives to petroleum- A shot survey of potential oil crop platforms. *Biochimie*, 91:665-670.
- COQUEREL, Y. & RODRIQUEZ, J. 2008. Microwave-assisted Olefin Metathesis. *European Journal of Organic Chemistry*, 1125-1132.
- DJIGOUE, G.B. & MEIER, M.A.R. Improving the selectivity for the synthesis of two renewable platform chemicals via olefin metathesis. *Applied Catalysis A: General*, 368:158-162.
- DME (Department of minerals and energy). 2005. Energy efficiency strategy for the republic of South Africa. Pretoria: Government Printer. 46p.
- EBERHARD, A. The future of South African Coal: Market, Investment and Policy challenges.
- FORMAN, G.S., BELLABARBA, R.M., TOOZE, R.P., SLAWIN, A.M.Z., KARCH, R. & WINDE, R. 2006. Metathesis of renewable unsaturated fatty acid esters catalysed by a phoban-indenylidene ruthenium catalyst. *Journal of organometallic chemistry*, 619:5513-5516.
- HUBER, G.W. & DUMESIC, J.A. 2006. An overview of aqueous-phase catalytic processes for production of hydrogen and alkanes in a biorefinery. *Catalyst Today*, 111:119-132.
- KNOTHE, G. 2008. "Designer" Biodiesel: Optimizing Fatty Ester Composition to Improve Fuel Properties. *Energy & Fuels*, 22:1358-1364.
- MARVEY, B.B. 2008. Sunflower-based feedstocks in non-food applications: Perspectives from olefin metathesis. *International journal of molecular sciences*, 9:282-1406. Aug.
- MARVEY, B.B., DU PLESSIS, J.A.K. & VOSLOO, H.C.M. 2005. The metathesis of polyunsaturated fatty esters using the homogeneous W(O-2,6-C₆H₃X₂)₂Cl₄/Me₄Sn catalytic systems. *Journal of molecular catalysis A: Chemical*, 214:151-157.
- SANCHEZ, O.J. & CARDONA, C.A. 2008. Trends in biotechnological production of fuel ethanol from different feedstocks, *Bioresource technology*, 99:5270-5295.
- SANFORD, M.S., LOVE, J.A. & GRUBBS, R.H. 2001. Mechanism and activity of ruthenium olefin metathesis catalysts. *Journal of the American chemical society*, 123:6543-6554.