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To be cited as: *ChemSusChem* 10.1002/cssc.201601824

Link to VoR: http://dx.doi.org/10.1002/cssc.201601824

A Journal of ChemPubSoc Europe

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Remarkably Efficient Microvawe-Assisted Cross-Metathesis of Lipids in Solvent Free Conditions

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ABSTRACT

Catalytic transformation of renewable feed stocks into fine chemicals is in high demands and olefin metathesis is one of the sophisticated tools for biomass conversion. Nevertheless, the large scale viability of such processes depends on the conversion efficiency, energy efficiency, catalytic activity, selective conversion into desired products and environmental footprint of the process. Thus, conversions of renewables using simple, swift, and efficient methods are desirable. A microwave-assisted ethenolysis and alkenolysis (using 1-5 hexadiene) of canola oil and methyl esters derived from canola oil (COME) and waste/recycled cooking oil (WOME) was carried out using ruthenium based catalytic systems. A systematic study using 1st and 2nd generation Grubbs (**G1**, **G2**) and Hoveyda-Grubbs (**HG1** & **HG2**) catalysts was carried out. Among all ruthenium catalysts, **HG2** was found to be highly active in the range of 0.002-0.1 mol% loadings. The conversions proved to be highly efficient with outstanding values of turnover numbers (TONs) and turnover frequencies (TOFs). The TONs and TOFs for ethenolysis of COME (~1.5 million & 26,000), direct ethenolysis of canola oil (~0.6 million & 10,300), for WOME (>1 million & 17,900) and for cross metathesis of 1,5-hexadiene with COME (1.6 million & 27,500) were achieved. The ethenolysis of commercial methyl oleate was also performed leading to TONs ~1.2 million and TOFs 20,300 s^{-1} under microwave conditions.

INTRODUCTION

More than 90% of the raw materials for today's chemical industry are fossil feedstocks in the form of oil and gas.[1] Roughly one-tenth of the feedstock comes from renewable resources.[2] Considering the dwindling fossil fuel resources and increasing importance of sustainability, chemical industry and academia has focused interest on the development of fuels, chemicals and materials from renewable resources.[3] Therefore, in order to achieve more sustainable economy, the transition from petrorefinery to biorefinery is required.[4] Particularly transformation of vegetable oils, due to their low cost, biodegradability and large scale availability, has received renewed attention.[5] In 2012-2013, the world supply and distribution of major oil seeds was 462 million metric tons including palm, canola, sunflower and soy bean respectively.[6] In addition to large scale availability, a wide range of products can be obtained from seed oils which make them cost-effective and environment friendly alternative.[3b, 7] These attributes make oils a good fit for a biorefinery which mimics a traditional petrochemical paradigm.[8]

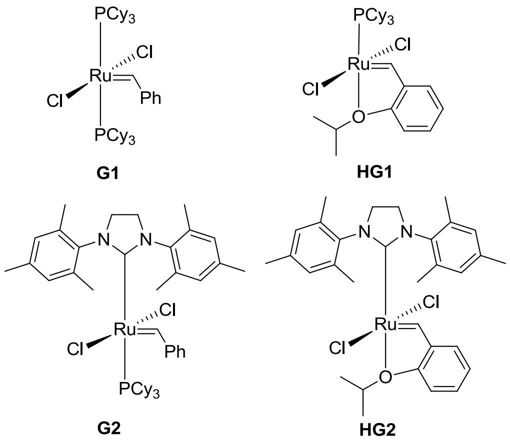
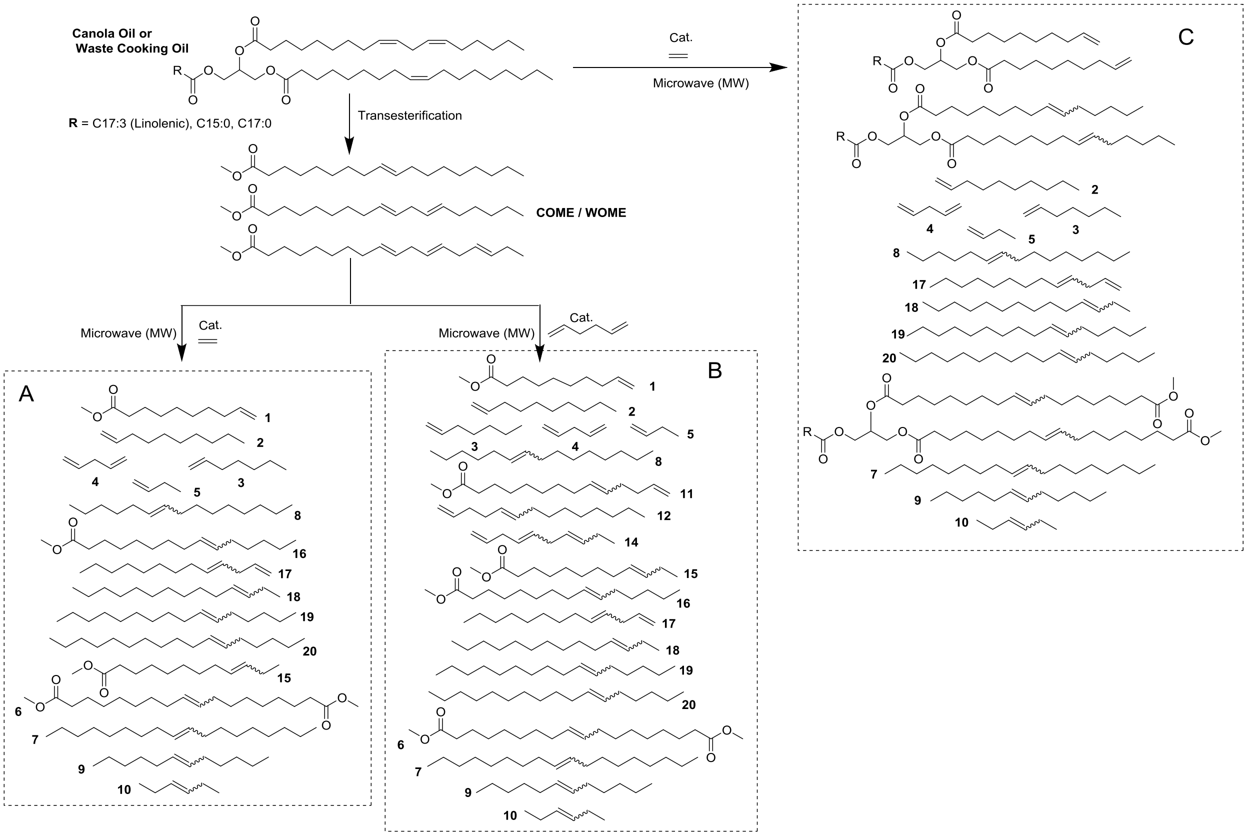


Figure 1. The Grubbs (**G**) and Hoveyda-Grubbs (**HG**) first and second generation (**1** & **2**) catalysts used for ethenolysis and alkenolysis.

For chemical conversion and formation of new carbon–carbon double bonds, olefin metathesis is considered one of the most versatile and powerful synthetic transformation tools and has been used in both pure and applied chemistry.[9] The transformative progress in pure and applied chemistry through metathesis was recognized in 2005 with the award of the Nobel Prize in Chemistry.[10] Generally olefin metathesis can be classified into ring-opening, ring closing and cross-metathesis.[11] Metal-catalyzed olefin cross-metathesis has become a standard synthetic method with numerous industrial uses, including the well-known Shell Higher Olefin Process (SHOP).[12] Olefin cross-metathesis is a catalytic reaction between two alkene molecules that results in redistribution of alkylidene groups.[13] The cross-metathesis of an olefinic compound with ethylene is called ethenolysis and a cross-metathesis with an olefin other than ethylene is called alkenolysis.[6, 14] Various efforts have been made on the conversion of plant oil derived fatty acids into products using ethenolysis chemistry.[14-15] The production of olefins through ethenolysis, the cross metathesis (CM), has been target of many investigations because this process produces high value linear α-olefins which are direct antecedents to various applications including monomers for polymer synthesis, cosmetic ingredients, lubricants, detergents, soaps, perfumes, antimicrobial agents and renewable fuels.[16] The ethenolysis as well as alkenolysis of seed-oil derivatives and purified methyl oleate as a model substrate has been investigated.[16b, 17] However, generally reactions are carried out in organic solvents and a high catalyst loading is required for effective conversion particularly the ethenolysis.[17a, 17b, 17d, 18] The catalyst turnover numbers (TONs) greater than 50,000 are required for this process to be viable on larger scale.[17e, 19] Most of the studies reported to date have used purified methyl oleate as a model substrate for metathesis. Although high TONs have been reported on the alkenolysis of methyl oleate (MO) and FAMEs using other olefins as ethylene surrogates and proved to be commercially viable leading to large scale manufacturing facility.[6, 20] For example, the TONs as high as 192,900 and 470,000 for CM of methyl oleate with propylene and 2-butene have been achieved.[17e, 21] Nevertheless, the metathesis with higher olefins results in the production of substantial amount of internal olefins which are considered low value products compared to α-olefins produced through ethenolysis.[16b] Therefore, recent investigations have been focused on the conversion of methyl oleate into high value terminal products using ethylene in the presence of different catalysts in organic solvents.[17a, 18b, 22] More recently, the ethenolysis TONs as high as 340,000 have been achieved using newly synthesized cyclic alkyl amino carbene (CAAC) complexes[16b]and ethenolysis using efficient molybdenum and tungsten based catalysts have been reported.[23] Despite the substantial improvements in the metathesis, the solvent free rapid conversion of plant oils into desired terminal olefins is undoubtedly an important concept for efficient conversions of plant oil feedstocks into multiple downstream products.



Scheme 1. Products of ethenolysis (A); alkenolysis (B) of canola oil methyl esters (COME) waste cooking oil methyl esters (WOME) and direct ethenolysis of canola oil (C) under microwave conditions

Microwaves are considered as green, rapid and environment friendly due to low energy consumption[24] and lead to enhanced rates, yields, and purities in comparison to reactions conducted with conventional heating.[25] There has been great success in the field of microwave-assisted organic synthesis, polymer chemistry, material sciences, nanotechnology, and biochemical processes.[26] Despite few reports on metathesis particularly ring-closing metathesis of small molecules,[26a, 26b, 27] to the best of our knowledge, the microwave-assisted metathesis particularly ethenolysis of natural oils has not been investigated.

Herein, we report the ethenolysis and alkenolysis of canola oil, methyl esters of canola oil (COME) and waste/recycled cooking oil (WOME) using ruthenium metathesis catalysts (Figure 1) under microwave irradiation conditions.

RESULTS AND DISCUSSION:

Olefin metathesis (OM) is very popular and useful reaction in chemical synthesis. Recently, use of OM for the conversion of oleochemicals into valuable products has triggered an explosive growth of interest due to introduction of the well-defined, functional-group tolerant ruthenium alkylidene complexes developed by Grubbs and coworkers.[28] Although these catalysts can be handled in air and react selectively with olefins in the presence of various functional groups.[10a, 29] The efficiency of an olefin metathesis catalyst is determined by the rate of metathesis over the rate of the catalyst decomposition.[30] The effects of temperature and solvents on catalyst efficiency and decomposition have been investigated.[31] The catalyst decomposition during extended reaction times and temperatures significantly affect TONs and product selectivity.[30] The selectivity of ruthenium complexes for the production of α-olefins has been reported as poor.[17a] With an aim of rapid conversion of canola oil and mixture of methyl esters COME and WOME into linear α-olefins under solvent free metathesis conditions, we investigated the microwave-assisted ethenolysis and alkenolysis using ethylene and a diolefin (1,5-hexadiene). The reaction conditions including temperature, time, catalysts screening and their concentrations were optimized. For oils and FAMEs complicated product mixtures are produced therefore TONs were calculated based on Me9DA (TON_{Me9DA}), a method particularly used for oils and FAMEs.[17e]

Catalyst Screening and Ethenolysis of COME

For ethenolysis reactions of COME, initially a group of four different ruthenium based catalysts **G1**, **G2**, **HG1** and **HG2** (Figure 1) was screened to assess their suitability under microwave irradiations at a temperature of 50°C for a time span of 8 minutes (3 minutes ramping time + 5 minutes hold time). The initial reactions were performed with catalyst loading of 0.1 mol%. As can be seen from table 1, the second generation catalysts (**G2** & **HG2**) displayed better transformation of reactants into metathesis products giving higher conversion rates (96%) (table 1, entry 2 and 10) as compared to first generation catalysts (**G1** & **HG1)** having conversion rates of 65% and 64% respectively with slightly higher GC% yield and TONs (table 1, entry 1 and 3). Considering higher conversion rates of second generation catalysts, the **G2** & **HG2** were further investigated using lower catalyst loading (0.05 mol%) and shorter reaction times of 3.5 minutes (3 minutes of ramping time + thirty seconds hold time). Despite 50% decrease in catalyst loadings of **G2** & **HG2**, the conversion rates did not change significantly (95% and 96% respectively). However, the decrease in yield for catalyst **G2** was observed (table 1, entry 4). Contrary to catalyst **G2**, the catalyst **HG2** displayed higher yield and improved TONs (318,300) and TOFs (table 1 and S1 entry 5). So, during the initial screening of four catalysts, **HG2** was found to be the most promising catalyst under solvent free microwave conditions. **HG2** catalyst was further studied at different temperatures (40, 50, 60 and 80°C) and with lower catalyst loadings to obtain best yield, TONs and TOFs. An efficient conversion (96%) was still reached at all temperatures with 0.1 mol% of **HG2** catalyst loading. A reaction temperature of 40°C provided less yield and TONs (table 1, entry 9), impeding the catalyst utility. While the ethenolysis at a temperature of 50°C was found to be most appropriate as compared to reactions conducted at 60°C and 80°C for the conversion of substrates into metathesis products (table 1). The reactions at increased temperature probably induced the early decomposition of catalyst, which may account for reduced TONs. These investigations indicate that the solvent free microwave-assisted metathesis reactions at lower or higher temperature than 50°C are of minimal benefits in terms of yield and TONs. Therefore the temperature of 50°C was found to be the most appropriate or optimal for metathesis reactions to get effective conversions.

Further ethenolysis reactions of COME were performed with lower concentration of **HG2** catalyst. Lowering the catalyst loading of **HG2** from 0.05 to 0.01 mol% resulted in a substantial increase in TONs (~1.5 million), TOFs (26,000 s^{-1}) (table 1 and S1 entry 6). By decreasing catalyst loading to 0.005 mol% (table 1, entry 7), it is worth noting that **HG2** still maintained higher conversion rate (95%), with slightly lower yield, TONs (~1.1 million) and TOFs (19400 s^{-1}) values. A significant decrease in conversion rate, TONs and TOFs was observed by lowering the concentration of **HG2** to 0.002 mol% (table 1 and S1 entry 8) suggesting that further decrease in catalyst is not useful. The possible terminal and internal olefins obtained after catalytic transformation of COME with ethylene are shown in scheme 1, and were characterized by GCMS analysis (figure 2). A fraction of volatile components was also collected after reaction completion and identified by GCMS (figure S1). For complete identification of all liquid components, the reaction mixture was subjected to silica gel column chromatography and obtained ethenolyzed hydrocarbons fraction (figure S2) and ethenolyzed methyl esters fraction (figure S3) were characterize by GCMS. The separated pure diester **6** (figure S6) was characterized by proton NMR.

Table 1. Ethenolysis of renewable canola methyl esters derived from canola oil.

Entry	Catalyst	Loading [mol%]	Temperature [°C]	Hold time [min.]	Conv. [%]	GC% yield of Me9DA	TON_{Me9DA}
1	G1	0.1	50	5	65	22.8	126,500
2	G2	0.1	50	5	96	24.4	130,900
3	HG1	0.1	50	5	64	34.7	263,500
4	G2	0.05	50	0.5	95	7.7	82,500
5	HG2	0.05	50	0.5	96	21.8	318,300
6	HG2	0.01	50	1	96	21.3	1,561,500
7	HG2	0.005	50	1	95	16	1,165,600
8	HG2	0.002	50	1	69	9.4	573,300
9	HG2	0.1	40	3	96	18.7	136,200
10	HG2	0.1	50	1	96	22.7	165,000
11	HG2	0.1	60	1	96	20.6	150,100
12	HG2	0.1	80	1	96	23.6	171,700

Although increased TONs from ~0.16 million to ~1.5 million without decrease in conversion rate was achieved by lowering the catalyst loading from 0.1 mol% to 0.002 mol%, but yield gradually decreased as depicted in table 1. It has also been observed that decrease in reaction times under microwave irradiation resulted in unprecedented TOFs 26,000 s^{-1} (table S1, entry 6).

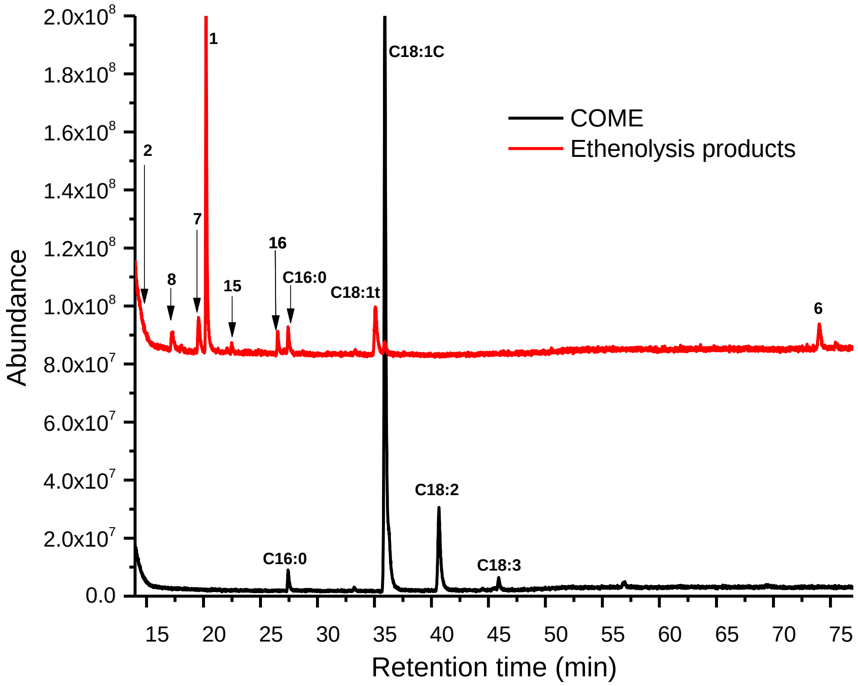


Figure 2. GCMS spectrum of canola oil methyl esters (COME) and ethenolysis products

Investigation on Ethenolysis of WOME

Ethenolysis of WOME was carried out using conditions already optimized for ethenolysis of COME but using different concentrations of **HG2** (table 2). The conversion of 96% was observed using different catalyst loadings from 0.1 mol% to 0.005 mol%. With 0.1 mol% of catalyst loading ~0.1 million TONs and 1790 s^{-1} TOFs were achieved. Decreasing the catalyst contents to 0.005 mol% still provided TONs (~1.0 million) and TOFs (17,900 s^{-1}) as shown in table 2 and S2, entry 3. The product components obtained after ethenolysis of WOME were characterized by GC analysis (figure 3) and found to be similar to those described for the ethenolysis of COME (scheme 1).

10.1002/cssc.201601824

Table 2. Ethenolysis of methyl fatty esters (WOME) derived from waste cooking oil.

Entry	Catalyst	Loading [mol%]	Temperature [°C]	Hold time [min.]	Conv. [%]	GC% yield of Me9DA	TON$_{\mathrm{Me9DA}}$
1	HG2	0.1	50	1	96	14.7	107,500
2	HG2	0.05	50	1	96	14.0	205,200
3	HG2	0.005	50	1	96	14.7	1,078,100

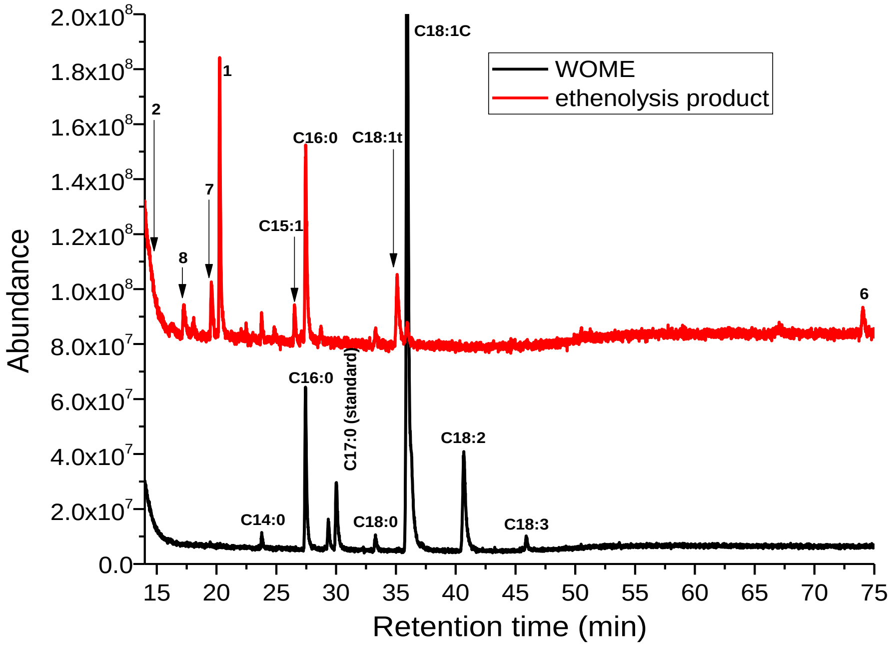


Figure 3. GCMS spectrum of waste cooking oil methyl esters (WOME) and its metathesis products with ethylene

Study on Metathesis of COME with 1,5-Hexadiene

Alkenolysis, the cross metathesis reactions of longer chain internal and terminal olefins other than ethylene, have been investigated using propene, butene and octene with purified methyl oleate and FAMEs of different plant oils and higher TONs compared to ethenolysis have been reported.[17e, 19, 21, 31c] Despite higher TONs, alkenolysis with higher olefins results in significant amounts of undesired internal olefins.[16b] The cross-metathesis with diolefin such as 1,5-hexadiene should result in terminal metathesis products due to the presence of both terminal double bonds (figure 4). There are no reports in literature on the use of 1,5-hexadiene therefore alkenolysis of canola methyl esters with 1,5-hexadine was also performed using microwave radiations. Similar to ethenolysis, four catalysts **G1**, **G2**, **HG1** and **HG2** were screened with 0.1 mol% catalyst loadings at 50°C temperature. No reaction products were observed with 0.1 mol% of first generation catalysts (**G1** & **HG1**) for 8 minutes reaction time under microwave conditions. Surprisingly, second generation catalysts (**G2** & **HG2)** gave the highest conversion rate of 99% within ~ 8 minutes (~3 minutes of ramping time + 5 minutes hold time) with effective TONs of 84,100 and 133,800 respectively (table 4, entry 2 and 4). Both these catalysts were further studied at lower loading of 0.05 mol% for a reaction time of ~3.5 min (~ 3 min ramping time + 30 seconds hold time). Using catalyst **G2,** a sharp decrease in conversion rate and yield while slight increase in TONs was observed (table 3, entry 5). However, with **HG2**, the conversion rate was maintained at 99% with slightly lower yield and improved TONs as well as TOFs (table 3 and S3, entry 6). These results also suggest **HG2** as most effective catalyst for alkenolysis of fatty esters under microwave conditions.

The alkenolysis reactions were also carried out at 45°C, 60°C and 80°C using 0.1 mol% of **HG2** catalyst. At 45°C and 80°C, a good yield and TONs were obtained, but conversion rate was decreased to 82% and 93% respectively (table 1, entry 8 and 10). These results suggested 50°C as an optimal temperature for alkenolysis reactions.

Further alkenolysis reactions were carried out at 50°C at lower concentration of **HG2** catalyst. Decreasing the catalyst loading to 0.01 mol% still provided highest conversion rate and a remarkable increase in TONs (~1.6 million) and TOFs (27,500 s^{-1}) values (table 3 and S3, entry 7). Further lowering of catalyst below 0.01 mol% resulted in very low conversions for alkenolysis reactions.

Table 3. Cross metathesis of renewable FAME's derived from canola oil with 1,5-hexadiene.

Entry	Catalyst	Loading [mol%]	Temperature [°C]	Hold time [min.]	Conv. [%]	GC% yield of Me9DA	TON$_{Me9DA}$
1	G1	0.1	50	5	0	0	0
2	G2	0.1	50	5	99	15.6	84,100
3	HG1	0.1	50	5	0	0	0
4	HG2	0.1	50	5	99	18.4	133,800
5	G2	0.05	50	0.5	27	9.7	104,100
6	HG2	0.05	50	0.5	99	16.1	234,700
7	HG2	0.01	50	1	98	22.6	1,655,400
8	HG2	0.1	45	5	82	26.0	189,100
9	HG2	0.1	60	1	99	11.5	83,600
10	HG2	0.1	80	1	93	27.0	196,400

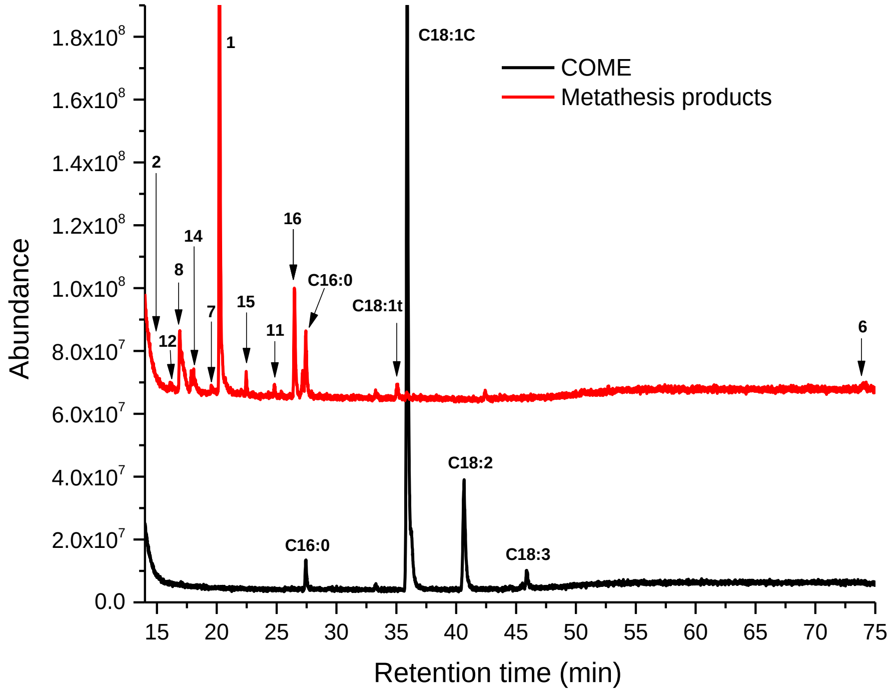


Figure 4. GCMS spectrum of COME and alkenolysis products

Direct Ethenolysis of Canola Oil

Direct ethenolysis of canola oil was also studied under similar conditions as described above for ethenolysis of COME. More than 94% conversions were obtained (table 4) with two different loadings of **HG2** catalyst (0.05 mol%, and 0.01 mol%). Anomalous behavior can be seen in table 4, despite higher conversion rate, due to substantial transformation of *cis*-oleate (C18:1 C, figure 5) to *trans*-oleate (C18:1 t) lower yield was obtained. A notable increase in TONs (form 48,400 to 618,700) and TOFs (from 800 to 10,300 s^{-1}) were observed when catalyst was decreased from 0.05 mol% to 0.01 mol% (table 4 and S4). The raw product mixture obtained after ethenolysis (Scheme 1C) was transesterified with methanol prior to its characterization with GCMS (figure 5). The products obtained were similar to those obtained for ethenolysis of COME.

Table 4. Ethenolysis of canola oil (TAG's).

Entry	Catalyst	Loading [mol%]	Temperature [°C]	Hold time [min.]	Conv. [%]	GC% yield of Me9DA	TON_{Me9DA}
1	HG2	0.05	50	1	95	1.1	48,400
2	HG2	0.01	50	1	94	5.7	618,700

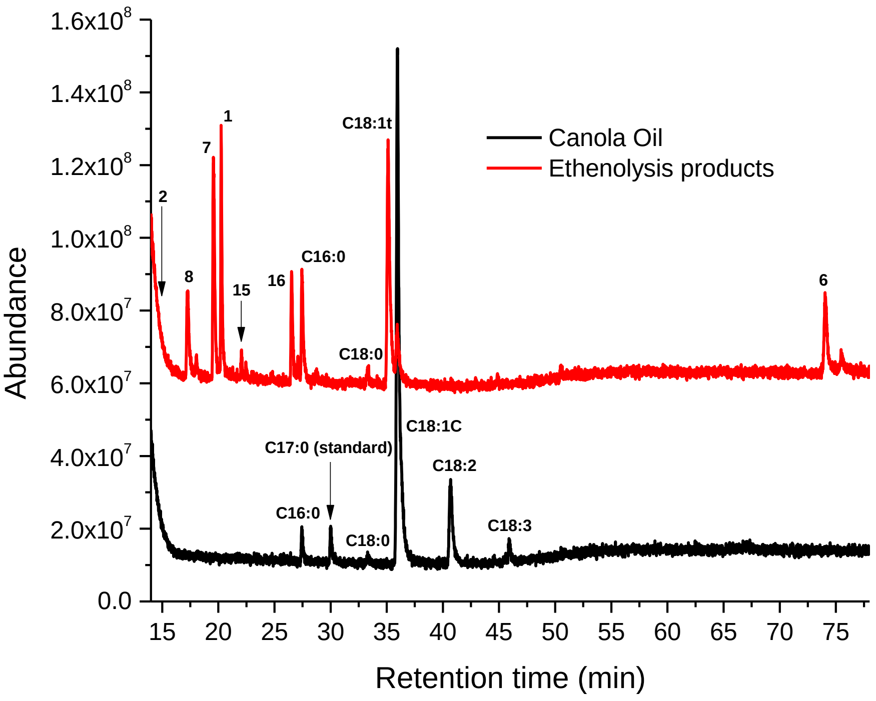


Figure 5. GCMS spectrum of canola oil and its ethenolyzed products after transesterification with methanol.

Methyl Oleate Ethenolysis

An extensive work has been reported on ethenolysis of methyl oleate[15a, 18b, 32]. To compare the ethenolysis results of renewable fatty esters, ethenolysis of methyl oleate was performed using similar conditions as described for canola oil methyl esters. Cross metathesis of methyl oleate with ethylene results in the formation of two cross products, methyl 9-decenoate (**1**) and 1-decene **(2**) and two self-products dimethyl 9-octadecene-1,18-dioate (**6**) and 9-octadecene (**7**) as presented in scheme 1. Ethenolysis of methyl oleate was conducted using **HG2** catalyst with two different concentrations of 0.005 and 0.01 mol% providing almost 94% conversion in all cases (table 5). The highest value of TONs (~1.2 million) were obtained with 0.01 mol% loading of catalyst (table 5, entry 3), whereas decreasing catalyst loading to 0.005 mol%, a substantial decrease in yield and TONs were observed (table 5, entry 2). The less yield and TONs even with higher conversion rate in case of 0.005 mol% loading of catalyst are due to formation of trans methyl oleate during the reaction. A good number of TOFs values were also observed in ethenolysis of methyl oleate (table S5) providing the highest TOFs value of 20,300 s^{-1} with catalyst loading of 0.01 mol% (table S5, entry 3).

From the results (table 5), it can be seen that ethenolysis of methyl oleate displayed less conversion rate, yield and TONs compared to ethenolysis of COME. With catalyst loading of 0.01 mol%, the observed ethenolysis TONs (1.2 million) for methyl oleate (table 5, entry 3) were found to be 20% less than the TONs (1.5 million) obtained after ethenolysis of COME (table 1, entry 6). During ethenolysis of methyl oleate, lowering the catalyst loading to 0.005 mol% resulted in a significant decrease in TONs to 0.79 million (table 5, entry 2), while ethenolysis of

COME still displayed an efficient value of 1.16 million, (table 1, entry 7). The less conversions rate, yield and TONs in case of methyl oleate ethenolysis can be attributed to less purity of methyl oleate (commercial MO without purification was used) which affects the efficiency of reaction[33].

Table 5. Ethenolysis of methyl oleate.

Entry	Catalyst	Loading [mol%]	Temperature [°C]	Hold time [min.]	[a]Conv. [%]	GC% yield of Me9DA	TON$_{Me9DA}$
1	HG2	0.005	50	1	94	3.9	372,300
2	HG2	0.005	50	1	94	8.3	794,200
3	HG2	0.01	50	1	94	12.8	1,222,800
4	HG2	0.01	50	1	92	10.2	972,300

Conclusion

Use of microwave electromagnetic radiations for the CM of fatty esters of vegetable oils with ethylene and 1,5-hexadiene brought a dramatic increase in the conversion rates, TONs and TOFs in a very short reaction time under solvent free conditions and low catalysts loadings. Ethenolysis of WOME also provided promising results. Among four catalysts, **HG2** was found to be most promising catalyst at 50°C generally providing efficient conversions and TONs during ethenolysis and alkenolysis reactions. Unprecedentedly, more than 1.5 million TONs and up to 26,000 s^{-1} TOFs for ethenolysis of COME, around ~0.6 million TONs and 10,300 s^{-1} TOFs for direct ethenolysis of canola oil, above one million TONs and 17900 s^{-1} TOFs for ethenolysis of WOME, more than 1.6 million TONs and above 27,500 s^{-1} TOFs for the cross metathesis of 1,5-hexadiene with COME were achieved. Ethenolysis of methyl oleate was also performed for comparison with COME and WOME. The highest value of TONs ~1.2 million and TOFs 20,300 s^{-1} were also attained for the ethenolysis of methyl oleate. These results demonstrate that microwave-assisted conversion of renewable oils and their fatty acid derivatives could be an appropriate and rapid process for the production of various starting materials for the chemical industry.

EXPERIMENTAL

General Considerations

All of the reactions were performed on a CEM-Discover (120 V, Matthews, USA), a source of microwave irradiation in 10 mL sealed tube, while infrared mode was used to measure the temperature of the reaction contents. To identify the components, GC-MS analyses of all samples were conducted on Agilent 6890N (USA) gas chromatograph, fitted with a fused silica capillary column SP2560 (100m × 0.25mm × 0.2 μm film thickness) and detector 5975B inert XL MSD. The sample volume of 2 μL was injected, the injector temperature was set to 240 °C and a split mode with ratio of 20:1 was used. The initial temperature of oven was set to 45 °C and held for 4 minutes. The temperature was then increased to 175 °C with a ramp rate of 13 °C min^{-1}; held for 27 minutes and further ramped at 4 °C min^{-1} to 215 °C and held for 35 minutes. The mass scanning range of 30-1000 amu at 1.55 scan per second was performed. Helium gas was used as a mobile phase with a constant flow rate of 1.3 mL/min.

They hydrocarbon fractions were characterized on Agilent 7980A (USA) instrument using HP5 column (30m × 0.32mm × 0.25 μm film thickness), coupled with inert EI MSD with triple axis detector (5975C, Agilent, USA). The injection volume of 1 μL was used with injector temperature of 250 °C in a splitless mode. The oven initial temperature of 50 °C was set and held for two minutes. The temperature was increased at a ramp rate of 5°C min^{-1} to 325 °C and then held for five minutes. The MS scanning range of 50-600 amu was applied with a scan rate of 2.66 per second. A constant flow rate of 4.4 mL/min of helium gas was used as mobile phase.

While Perkin Elmer GC-FID Clarus 500 instrument (USA) equipped with flame ionization detector was used for quantitative analysis to measure the conversion rate, selectivity and yield of all samples. The temperature was set at 280 °C for detector, while 240 °C for injector. The air and hydrogen gases were used as a carrier with the flow rate of 450 and 45 mL/min respectively. The column used and all other conditions were same as mentioned above for GC-MS instrument Agilent 6890N.

^{1}H NMR spectra of selected samples were recorded after dissolving in deuterated chloroform at 400 MHz frequency on a Varian INOVA instrument at a temperature of 27 °C.

The conversion rates of all metathesis reaction were calculated using formula given below;

Conversions = 100 -[(final moles of reactants)100/(initial moles of reactants),

The turnover numbers (TONs) and turnover frequencies (TOFs) in all cases were calculated on methyl-9-deceneoate (Me9DA) bases reported below

TON_{Me9DA} (turnover numbers based on Me9DA) = 10,000 × (GC% yield of Me9DA)/(catalyst loading in mol ppm)

TOF_{Me9DA} = TONs / time (sec.).

Materials

Canola oil, methyl oleate (99%), Grubbs catalyst 1st generation (**G1**, 97%), Grubbs catalyst 2nd generation (**G2**), Hoveyda- Grubbs catalyst 1st generation (**HG1**), Hoveyda- Grubbs catalyst 2nd generation (**HG2**, 97%), 1,5-hexadiene (97%), ethyl vinyl ether (≥98%), potassium hydroxide (≥85%), sodium chloride (≥99.5%), anhydrous sodium sulphate (≥99%), methanol (≥99.8%) and acetone (≥99.9%) were obtained from sigma Aldrich. The ethylene gas (Mathesons, polymer grade, CAS: 74-85-1), silica gel used for column chromatography (70-230 mesh, 60 Å), flash silica (Silicycle, 40-63 μm, 230-400 mesh), thin layer aluminium chromatographic plates

(Macherey-Nagel, 0.20 mm thick, 20 × 20 cm size, UV254), ethyl acetate (fisher, 99.9%), n-hexane (Caledon) were purchased and used as such.

Methanolic Transesterification of Canola Oil and Waste Cooking Oil

Methanolic transesterification of canola oil and waste cooking oil into their fatty esters was performed using KOH as a base according to the previously reported method. [34]

Separation of Saturated Esters by Crystallization Method

For best results in metathesis reactions, saturated esters were removed from transesterified canola methyl esters (COME) and waste cooking oil methyl esters (WOME) by crystallization method. For their separation, these esters were dissolved in acetone and kept overnight at a temperature of -5°C. The volume of acetone used was equal to the volume of esters. The saturated esters get solidified at this lower temperature and were separated by filtration carried out at same temperature. This process was repeated three times to remove maximum amount of saturated esters. The obtained esters which were mostly unsaturated were dried and passed through a column of flash silica before proceeding for metathesis reactions.

General Procedure for Ethenolysis of Methyl Fatty Esters

Specific amount of methyl fatty esters were charged in a 10 mL glass vial having teflon coated stirring bar and was purged with nitrogen gas for five minutes. An appropriate amount of catalyst (table 1) was weighed in a glove box under an atmosphere of nitrogen and was added into the reaction vial. The reaction vial was sealed and brought to the ethylene line. The reaction vessel was purged with ethylene gas for five minutes and then ethylene was liquefied into the reaction vial to a volume of about 0.5 mL by cooling the vial in liquid nitrogen. The reactions were conducted in sealed reaction vessels at specified temperatures. The power is usually adapted by the instrument to reach and maintain the set temperature. The reactions in duplicate and in some cases in triplicate runs were carried out. The pressure variation during ethenolysis was between 5.5 bar to 8.3 bar, with an average pressure of 6.9 bar. The set maximum power for the instrument was 250 W. The reaction was run for specific time interval at a suitable temperature to get maximum conversions of reactants into product components. The ramp time to attain the required temperature was ~ 3 minutes. After reaction completion, ethyl vinyl ether (0.5 mL) was added into the reaction mixture to deactivate the catalyst and was passed through a plug of flash silica to remove the catalyst. The product components were characterized by GCMS and quantified with GC-FID by considering naturally occurring methyl palmitate (C16:0) in the canola oil and/or methyl heptadecanoate (C17:0) as an internal standard.

Ethenolysis of Canola Oil

Canola oil was first passed through a column of flash silica and anhydrous magnesium sulphate to remove colored pigments and moisture contents. Afterwards, it was proceeded for cross metathesis reactions with ethylene in the presence of catalyst **HG2** using identical conditions and/or methodology as mentioned for ethenolysis of methyl fatty esters. The obtained metathesis products were transesterified with methanol prior to GC analysis used for characterization and quantification of product components.

Separation of Components after ethenolysis of COME

A volatile fraction was collected right after the completion of ethenolysis reaction containing 1,4-petadiene (**4**) and 1-butene (**5**) and was characterized by GCMS (figure S1). The remaining mixture of ethenolyzed components were separated into three major fractions; ethenolyzed hydrocarbons fraction (EHF), ethenolyzed methyl esters fraction (EMEF) and pure dimethyl octadec-9-enedioate (**6**) with the help of silica gel column chromatography using an eluent system of 1-5% ethyl acetate in hexane. These fractions were further characterized by GCMS (figure S2 and S3). The hydrocarbon and methyl esters fractions were subjected to distillation separately to purify some of the major components. ^{1}H NMR of those purified components is provided in the supporting information (figures S4, S5 and S6).

Cross Metathesis of Canola Oil Methyl Esters with 1,5-Hexadiene

In a glove box under an inert atmosphere, an appropriate amount of catalyst (table. 4) was weighed and added into the reaction vial containing purified canola methyl esters (1 Eq.) degassed with nitrogen and equipped with a stirring bar. The reaction vessel was sealed and purged with nitrogen gas for five minutes followed by the addition of 1,5-hexadiene (2 Eq.) with the help of purged glass syringe. The sealed reaction vessel was placed in a microwave reactor under similar reaction conditions as described above for ethenolysis of methyl fatty esters. After reaction completion, ethyl vinyl ether (0.5 mL) was added into the reaction mixture to deactivate the catalyst and was passed through a plug of flash silica to remove the catalyst contents. The product components were characterized by GCMS and quantified with GC-FID by considering naturally occurring methyl palmitate (C16:0) in the canola oil and methyl heptadecanoate (C17:0) as an internal standard.

Acknowledgements Authors gratefully acknowledge the financial support for current work by The Alberta Innovates Bio Solutions (AI Bio).

Supporting Information

The GCMS plots for the volatile components, ethenolyzed hydrocarbons fraction (EHF), ethenolyzed methyl esters fraction (EMEF), TOF's table of all metathesis reactions and proton NMR spectra of purified components **1**, **6** and 7 are provided.

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Graphical Abstract

Remarkably Efficient Microvawe-Assisted Cross-Metathesis of Lipids in Solvent Free Conditions

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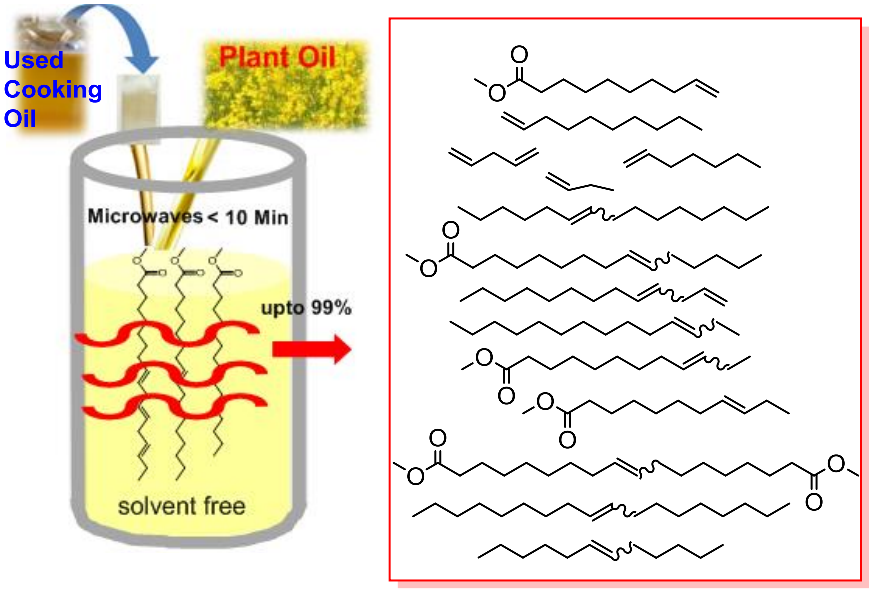

Rapid and effective conversion of lipids: A swift solvent free conversion of lipids into multiple high value products based on microwave-assisted metathesis approach is developed. The high conversions (upto 99%) were achieved within few minutes. The unprecedented turnover numbers and turnover frequencies for ethenolysis of canola esters (~1.5 million & 26,000), canola oil (~0.6 million & 10,300), and waste cooking oil (~ 1 million & 17,900) and for alkenolysis of canola esters (~1.6 million &, 27500) were achieved.