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## Cross metathesis of plant oil: A mini review on reaction condition and catalysis

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# Cross metathesis of plant oil: A mini review on reaction condition and catalysis

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**Abstract.** The extensive use of the renewable plant oil-derived polyols could be hindered by its low hydroxyl value owing to the oil saturation level and structural limitations. In recent years, olefin cross-metathesis has turned out to be one of the attractive methods to overcome this constraint by redistributing alkene fragments and regenerating carbon-carbon double bonds in the plant oil. The product distribution of the cross-metathesis of plant oil is significantly influenced by the types of catalysts and olefin as well as reaction conditions. Accordingly, dissimilar from the extensive reviews on the types of bio-based feedstocks and catalysts for cross metathesis, this article evaluates in specific the operating condition of cross-metathesising the plant oils using different olefins and catalysts, aiming to identify the future research avenues in developing a more technical feasible process to value add the plant oil. It is anticipated that the product yield resulted from the cross-metathesis of another potential feedstocks, the palm oil could be increased within a practical timeframe using 1-propene or 1-octene with a temperature not more than 60 °C and catalyst loading in ppm level.

## 1. Introduction

The production of polyurethane (PU) from renewable and biodegradable feedstock has been intensively researched because of the increased awareness of sustainable and environmentally benign development [1]. Commonly, PU is produced through a polyaddition reaction between the petroleum-based polyol with terminal hydroxyl groups (soft segment) and the diisocyanate (hard segment) [2]. Polyol is accountable for the flexibility and elastomeric character of PU and it is the potential to be substituted by the green polyol derived from the plant oil [3-6].

Despite the renewable and environmentally friendly characteristics of plant oil, the non-terminal double bond of its original molecular structure could lead to the polyol of very low hydroxyl value (OHV) [7-8]. To produce the polyol with higher OHV value, the triglyceride structure of plant oil could be modified through self-metathesis, cross-metathesis, acyclic diene metathesis polymerization to redistribute the alkene fragments and regenerate carbon-carbon double bonds [9].

In comparison to self-metathesis, cross-metathesis of plant oil using external alkene (Alkenolysis) can yield compounds with increased molecular diversity and reactivity that is more suitably used as the feedstock for the formulation of bio-based materials, particularly polyols for polyurethanes (PUs) production [10]. During this energetically neutral reaction, the double bonds present in triglycerides are cleaved by external alkene source hence producing shorter chain compounds with terminal double bonds [11]. The products obtained from the cross-metathesis of plant oil will have primary hydroxyl groups but no dangling chains, ascribing to the complete crosslinked and stronger PU networks [12-13].



Due to the high selectivity and activity of the homogeneous ruthenium-based catalyst, it is commonly used in the plant oil cross-metathesis (CM) to significantly improve the turnover numbers (TONs) of the reaction [14-15]. Nevertheless, it was reported that the ruthenium-based catalyst could be deactivated by the immediate product formed between the catalyst and the short-chain olefin [16-17]. In addition to the type of catalysts, the product distribution of the cross-metathesis of plant oil is also depending on the reaction conditions such as temperature, catalyst loading, etc [18-19]. With the intention to identify the opportunities in the future research, the present paper reviews the types of plant oils, the types of catalysts and followed by the operating conditions like catalyst loading, reaction temperature and reaction time adopted in the cross-metathesis using different olefins.

## 2. Types of plant oil modified through cross-metathesis

Since the past few decades, different types of plant oil have been modified through the cross-metathesis process with the purpose to convert it to the compounds with lower molecular weight and fatty acid chain structure comprising terminal double bonds, which are more suitable to be used as the feedstock for polyol production [20]. CM with lower olefins of distinct plant oils offers an attractive and non-destructive route from natural fats and oils consisting of long-chain fatty-acid triglycerides with isolated C=C bonds into fatty oils of lower molecular weight for wider applications [21-22].

The improved PU mechanical properties and deformation recovery ability when the polyol derived from the 1-butene cross-metathesized canola oil (CMTAG) was employed. Canola oil is a highly unsaturated commodity oil typically composed of ~92% unsaturated fatty acids (UFA) of which ~66% are monounsaturated fatty acids (MUFA) and 26% polyunsaturated fatty acids (PUFA), and ~8% saturated fatty acid (SFA) [23-24]. The structure of triacylglycerol (TAG) in the canola oil was radically transformed during cross-metathesis, leading to 40% oligomers, the shortened molecular structures (~50% of the UFA was cleaved at the double bonds) and an increased number of terminal double bonds (50% of total) [25-26]. In comparison to the original canola oil, CMTAG with a higher degree of unsaturation was more reactive and easily fully functionalized to polyol.

Butenolysis of different types of plant oil such as sunflower oil, canola oil, soybean oil and linseed oil were carried out by using Second-generation Hoveyda Grubbs catalyst [27]. CM of plant oils comprised of MUFA, oleic acid (C18:1) produced desired products such as glyceryl tri-9-undecenoate and 2-undecene [28]. Meanwhile, the CM of plant oils with PUFA such as linoleic acid (C18:2) and linolenic acid (C18:3) generated the preferred products non-ester alkenes such as 2,5-heptadiene, 2-octene and 2-pentene in addition to the fatty acid triglyceride with shorter chain length like glyceryl tri-9-undecenoate [29-30]. The CM of sunflower oil and sunflower oil had achieved a comparable TON due to its identical degree of unsaturation. Sunflower oil consists of 81% of C18:1 and 10% of C18:2 while canola oil comprises of 63% of C18:1; 18% of C18:2 and 11% of C18:3 [31-32]. Relatively, the TON attained in the CM of soybean oil and linseed oil was lower attributed to the lower degree of unsaturation. Soybean oil with 83% of unsaturated triglycerides is dominated by 54% of C18:2 whereas the linseed oil comprised of 88% of unsaturated triglycerides is constituted by 53% of the major component, C18:3 [30,33].

The effect of degree of unsaturation of the oil was also verified by in the cross metathesis of different types of plant oil using 1-butene and 50 ppm of C627 (Second-generation Hoveyda-Grubbs) catalyst [34,35]. The TON achieved in the reaction using sunflower oil was the highest followed by cross metathesis using olive oil, castor oil and peanut oil. The reaction performance is closely corresponded to the degree of unsaturation of the plant oil as arranged in a descending order as follows: castor oil (97.9%)> sunflower oil (91%)> olive oil (84.9%)> peanut oil (80.11%). It needs to emphasise that the castor oil could not outperform the sunflower oil despite its higher degree of unsaturation attributes to the presence of hydroxyl unsaturated fatty acid, ricin oleic acid (95.1%).

The soybean oil treated with magnesol for the removal of impurities prior to the propenolysis at 60°C for 4 hrs had resulted a yield of 55%, approximately 38% rises from the yield obtained from cross metathesis of untreated soybean oil [35]. In addition, the use of 1-octene rather than ethylene in the CM of soybean oil had significantly increase the TON of the reaction catalysed by C627 and C827 (an N-

heterocyclic carbene containing ruthenium-based catalyst) catalysts [36]. The poor performance of the ethenolysis of soybean oil could be ascribed to the formation of ruthenium methylidene, a catalytic intermediate, from the reaction of ruthenium-based catalysts with ethylene that would further decompose to a catalyst that promotes double-bond isomerization [23,37].

The resultant products from the CM of different types of plant oil are summarised in Table 1. It can be found that technical information about the CM of palm oil is scarcely reported in the open literature even though it is a potential feedstock for CM with its 50% unsaturated fatty acid composition. Therefore, it should be considered for further research to derive more value-added products from palm oil.

### 3. Types of catalysts used for plant oil cross-metathesis

A catalyst is a substance that is used to increase the rate of the reaction. Catalyst is primarily classified into four types namely homogeneous, heterogeneous (solid), heterogenized homogeneous catalyst and biocatalyst [39,40]. Owing to the potential industrial importance of CM reaction, a lot of efforts have been devoted for the development of catalyst.

Most of the works on cross-metathesis of plant oils with simple alkenes have been carried out using homogeneous ruthenium-based catalysts [12]. To a wide variety of interesting catalyst, Second-generation Grubbs ruthenium catalyst and Hoveyda-Grubbs catalyst outperforms the others to give comparably high yield due to its excellent catalytic stability and activity for CM reaction [39]. The second-generation ruthenium-based metathesis catalysts with high functional group tolerance have allowed the CM reactions with more-demanding reaction partners like electron-deficient or functional-group-containing olefins [35].

The CM of soybean oil in an excess of 1-octene at 40°C for 6 hrs using different types of catalysts with the concentration of 9 ppm. It was found that the Second-generation Grubbs catalyst (C848) and the C827 catalyst had similar performance and resulted higher TON as compared to the Second-generation Hoveyda-Grubbs catalyst (C627) [39]. The C827 catalyst was also proven superior to the C627 catalyst in catalysing the butenolysis of sunflower oil in the excess of 1-butene at 60°C and 70 psi for 4 hrs. Ruthenium metathesis catalyst which contains N-heterocyclic carbenes (NHCs) is divided into four sections namely the catalyst stereochemistry, the ruthenium carbene, the liable L ligand, and the NHCs. Ruthenium methylidene a catalytic intermediate is known to decompose rapidly through the insertion of n-aryl substituent into the methylidene carbene which subsequently generates various ruthenium hydrides that are inactive in metathesis transformation. The presence of NHCs is anticipated to increase the electron density at ruthenium for stabilizing the otherwise highly reactive and electron-deficient methylidene intermediate [41]. On the other hands, the Second-generation Hoveyda-Grubbs catalyst outperformed the ruthenium-based catalyst containing two 3-bromopyridine ligands when it was compared in the cross metathesis of triolein using 2-butene at ambient temperature and atmospheric pressure [42].

Thus far, the heterogeneous catalyst has only been employed in the CM of fatty acid methyl ester but not the CM of plant oil. The use of heterogeneous catalyst could overcome the issues of high costs and facile decomposition that hinders the recycling and regeneration of homogeneous catalysts [43-46] and hence worth exploring for the CM of plant oil.

**Table 1.** Cross metathesis of plant oils at different operating parameters.

No.	Type of plant oil and Olefin/ Ratio (mole olefin: mole double bonds)	Catalyst/Catalyst loading (ppm)	Temperature (°C)/ Pressure (psi)	Time (hrs)	Max. yield (%) / TON	Main product	References
1	Palm oil+butene	Grubbs ruthenium			NA	1-decene; 3,4-dodecene; glyceryl triundecanoate; glyceryl triundecanoate	[18]
2	Canola oil + 1-butene	Grubbs ruthenium	55 <sup>a</sup> /NA	24	NA	Olefin, TAG monomers 40%, TAG dimers, and trimers 40%, TAG oligomers, 10% (more than 50% with terminal double bond)	[25]
3	Canola oil +2-butene	Second-generation Hoveyda–Grubbs Catalyst <sup>b</sup> 25 ppm	Ambient temperature/ atmospheric pressure	18	NA/3.70x10 <sup>4</sup>	Glyceryl tri-9-undecenoate and non-ester alkenes such as 2,5-heptadiene, 2-octene, 2-pentene and 2-undecene	[30]
4	Linseed oil+2-butene	Second-generation Hoveyda–Grubbs Catalyst <sup>b</sup> 40 ppm	Ambient temperature/ atmospheric pressure	18	NA/2.30x10 <sup>4</sup>	Glyceryl tri-9-undecenoate and non-ester alkenes such as 2,5-heptadiene, 2-octene, 2-pentene and 2-undecene	[30]
5	Soybean oil+2-butene/ 10:1	Second-generation Hoveyda–Grubbs Catalyst <sup>b</sup> 40 ppm	Ambient temperature/ atmospheric pressure	18	NA/2.40x10 <sup>4</sup>	Glyceryl tri-9-undecenoate and non-ester alkenes such as 2,5-heptadiene, 2-octene, 2-pentene and 2-undecene	[30]
6	Triolein+2-butene/10:1	Second-generation Hoveyda–Grubbs Catalyst/10 ppm	Ambient temperature/ atmospheric pressure	4	92 <sup>c</sup> /9.30x10 <sup>4</sup>	Glyceryl tri-9-undecenoate and 2-undecene	[30]
7	Triolein+2-butene/10:1	Second-generation Hoveyda–Grubbs Catalyst/100 ppm		4 mins	95 <sup>c</sup> /NA		
8	Triolein+2-butene/10:1	Ruthenium based catalyst containing two 3-bromopyridine ligands/100 ppm		200 mins	95 <sup>c</sup> /NA		
9	Sunflower Oil + 2-butene/ 10:1	Second-generation Hoveyda–Grubbs Catalyst <sup>b</sup> 25 ppm	Ambient temperature	18	84/3.80x10 <sup>4</sup>	Glyceryl tri-9-undecenoate and non-ester alkenes such as 2,5-heptadiene, 2-octene and 2-undecene	[30]

**Table 1.** *continued*

No.	Type of plant oil and Olefin/ Ratio (mole olefin: mole double bonds)	Catalyst/Catalyst loading (ppm)	Temperature (°C)/ Pressure (psi)	Time (hrs)	Max. yield (%) / TON	Main product	References
10	Sunflower Oil + 1-butene/ 3:1	C827 (an N-heterocyclic carbene containing ruthenium-based catalyst) / 50 ppm	60/70	4	NA/7.70x10 <sup>3</sup>	Glyceryl tri-9-decenoate and non-ester alkenes	[38]
11	Sunflower Oil + 1-butene/ 3:1	C627 (Second-generation Hoveyda-Grubbs catalyst) / 50 ppm	60/70	4	NA/2.90x10 <sup>3</sup>	Glyceryl tri-9-decenoate and non-ester alkenes	[38]
12	Olive oil + 1-butene	627/50	60/70	4	NA/1.20x10 <sup>3</sup>	Glyceryl tri-9-decenoate and non-ester alkenes	[38]
13	Castor oil + 1-butene				NA/1.30x10 <sup>3</sup>		
14	Peanut oil + 1-butene				NA/2.00x10 <sup>2</sup>		
15	Soybean oil+ethylene/NA	C823 (First generation Grubbs Catalyst) / 111	40/100	6	NA/2.90x10 <sup>3</sup>	Glyceryl tri-9-decenoate and non-ester alkenes	[38]
16	Soybean oil+ethylene/NA	C827/10	40/150	6	NA/6.00x10 <sup>2</sup>		
17	Soybean oil+ethylene/NA	C627/22		6	NA/5.82x10 <sup>3</sup>		
18	Soybean oil+ethylene/NA	C712 (Ruthenium based catalyst containing ligand 3,5-diisopropylpyridine) / 22		6	NA/9.64x10 <sup>3</sup>		

**Table 1.** *continued*

No.	Type of plant oil and Olefin/ Ratio (mole olefin: mole double bonds)	Catalyst/Catalyst loading (ppm)	Temperature (°C)/ Pressure (psi)	Time (hrs)	Max. yield (%) / TON	Main product	References
19	Soybean oil+1-propene/NA	C827/75	60/130	2	35.74/4.76x10 <sup>4</sup>	Glyceryl tri-9-decenoate; undecenoate and non-ester alkenes such as 1-decene, 2-undecene	[38]
20	Soybean oil+1-propene/NA			4	39.08/5.20x10 <sup>3</sup>		
21	Soybean oil+1-propene/NA	C827/50	60/130	2	39.84/7.96x10 <sup>3</sup>		
22	Soybean oil+1-propene/NA			4	48.29/9.65x10 <sup>3</sup>		
23	Soybean oil+1-propene/NA	C827/25	60/130	1	46.64/1.86x10 <sup>4</sup>		
24	Soybean oil+1-propene/NA			2	48.39/1.93x10 <sup>4</sup>		
25	Soybean oil+1-propene/NA			3	51.54/2.06x10 <sup>4</sup>		
26	Soybean oil+1-propene/NA			4	52.86/2.11x10 <sup>4</sup>		
27	Soybean oil+1-propene/NA	C827/10	60/130	1	15.27/1.56x10 <sup>4</sup>		
28	Soybean oil+1-propene/NA			2	28.30/2.83x10 <sup>3</sup>		
29	Soybean oil+1-propene/NA			3	38.51/3.85x10 <sup>4</sup>		
30	Soybean oil+1-propene/NA			4	39.77/3.97x10 <sup>4</sup>		
31	Soybean oil+1-propene/NA			5	43.11/4.31x10 <sup>4</sup>		
32	Magnesol Treated Soybean oil + 1-propene/NA	C827/10	60/NA	4	55.10/4.98x10 <sup>4</sup>		

**Table 1.** *continued*

No.	Type of plant oil and Olefin/ Ratio (mole olefin: mole double bonds)	Catalyst/Catalyst loading (ppm)	Temperature (°C)/ Pressure (psi)	Time (hrs)	Max. yield (%) / TON	Main product	References
33	Soybean oil+1-octene/3:1	C848 (Second-generation Grubbs catalyst)/18	40/NA	6	NA/2.10x10 <sup>4</sup>	Glyceryl tri-9-decenoate and non-ester alkenes	[38]
34	Soybean oil+1-octene/3:1	C848/9	40/NA	6	NA/4.40x10 <sup>4</sup>		
35	Soybean oil+1-octene/3:1	C827/18	40/NA	6	NA/2.20x10 <sup>4</sup>		
36	Soybean oil+1-octene/3:1	C827/9	40/NA	6	NA/4.33x10 <sup>4</sup>		
37	Soybean oil+1-octene/3:1	C627/18	40/NA	6	NA/2.18x10 <sup>4</sup>		
38	Soybean oil+1-octene/3:1	C627/9	40/NA	6	NA/4.00x10 <sup>4</sup>		

<sup>a</sup> NA abbreviates not available.

<sup>b</sup> Catalyst loading in ppm calculated using the equation:

$$\text{ppm catalyst} = \frac{\text{moles catalyst}}{\text{moles olefinic substrate double bonds}} \times 1,000,000 \quad (1)$$

<sup>c</sup> This number denotes conversion.



#### 4. Important operating parameters for cross metathesis of plant oil

Considering the impacts of reaction conditions on the CM of plant oil, the present review covers the effect of important parameters such as catalyst loading, reaction temperature and reaction time on the reaction kinetics and product distribution.

##### 4.1. Catalyst loading

Catalyst loading is often defined as the molar ratio of the catalyst to the double bonds available in the triglyceride. It is a very important parameter to provide sufficient number of active sites to enable the occurrence of desired reaction [47]. To date, most of the researchers focused on the CM of fatty acid methyl ester such as methyl oleate using First- or Second-generation Grubbs catalyst, and pointed out that high conversions could only be achieved by the use of high catalyst loadings in a reasonable amount of time [39,48]. It was also discovered that the increase in catalyst loading had a significant effect on CM selectivity at all investigated temperature [42,49]. Generally, the loading of the metathesis catalyst adopted in the open literature is in the range of 1-5 mol% (1 mol%=10000 ppm). The catalyst loadings of as low as 1-5 ppm that resulted a turn over number (TON)>150000 was also reported in the studies involved highly pure reactants [15]. TON represents the total number of substrate molecules converted to the metathesis products per molecule of catalyst precursor under defined conditions up to the decay of activity. For industrial applications the TON is in the range  $10^6$ – $10^7$ [39]. To maintain a more practical and economical TON, the metathesis reaction that uses raw materials with impurities require higher catalyst loading and temperature that would eventually lead to the catalyst decomposition [50].

The CM of different types of plant oil was carried out and determined the effective turnover number (TON) as shown in Table 1. It was found that the TON of the CM of the model triglyceride, triolein was the highest (circa  $9.3 \times 10^4$ ) despite of the lowest catalyst loading (10 ppm) used in the reaction, in comparison to the cross metathesis of other plant oils [51]. It implies that the TON is influenced by the degree of unsaturation of the vegetable oil [43]. The vegetable oil with similar degree of unsaturation such as canola and sunflower oils as well as linseed and soy bean oils achieved the identical TON when these oils were cross metathesized, with higher TON ( $3.7$ – $3.8 \times 10^4$ ) acquired by the canola and sunflower oils owing to their relatively higher degree of unsaturation.

In the octenolysis of soybean oil catalysed by various types of catalysts, the increase of catalyst loading from 9 ppm to 18 ppm did not change the TON, implying an amount of 9 ppm of catalyst had provided sufficient number of active sites for the conversion the triglycerides with double bonds to the desired products such as tri-9-decenoate [38]. The same group of researchers had also carried out propenolysis of soybean oil using C827 (a ruthenium-based catalyst containing N-heterocyclic carbene) with various loadings ranged from 10-75 ppm. The highest yield, 52.86% was acquired in the reaction with the catalyst loading of 25 ppm [45]. Comparably, the use of 10 ppm and 75 ppm catalyst in the reaction had declined the yield about 26%. It evidences that an inadequate amount of catalyst does not provide sufficient active sites while the excess amount of catalyst promotes undesired side reactions [38]. To recapitulate, 1-octene and 1-propene are among the best olefins to give higher yield. The catalyst loadings ranged from 9-75 ppm have been adopted for the CM of plant oil with higher degree of unsaturation, in relative to the palm oil. It is expected that a higher catalyst loading is required in the palm oil cross metathesis and research should be carried out to validate the hypothesis.

##### 4.2. Reaction temperature

The reaction temperature though is an important parameter but its effect on the CM of plant oil using olefin has never been reported in the open literature. In the analogous reaction such as CM of fatty acid methyl ester using olefin, reaction temperature plays an imperative role in conversion, selectivity and the resulting yield [44]. The optimal reaction temperature depends on the types of catalyst, catalyst concentration and olefin concentration. Despite of the commonly known positive impact of the higher reaction temperature on the conversion, the conversion of the fatty acid methyl ester was adversely influenced by the reaction temperature when certain types of catalyst was employed. The increase of temperature had not only declined the conversion, but also the selectivity and yield of cross metathesis

products because of the elevated temperatures that promoted self-metathesis rather than cross metathesis. An intermediate temperature of 40-50°C was therefore recommended to suppress the side reactions [12]. Coincidentally to the CM of fatty acid methyl ester, the reaction temperature of the CM of plant oils lied between ambient temperatures to 60°C as indicated in Table 1.

#### 4.3. Reaction time

It is universally known that catalyst is introduced to speed up the rate of reaction and hence reducing the reaction time to ensure an economical viable and practical process. In comparison to other reaction conditions, reaction time was identified as one of the parameters with least influence on the performance of fatty acid methyl ester cross metathesis using ruthenium-based catalyst [12]. [38] manipulated the reaction time in their study on the propenolysis of soybean oil catalysed by C827 at 60°C and 130 psi. At the optimum catalyst loading of 25 ppm, the impact of reaction time was relatively less significant especially when the reaction time exceeded 3 hrs. The yield improvement was only 2% when the reaction time was prolonged from 3 hrs to 4 hrs. Nevertheless, a longer reaction time, 18-24 hrs was required to obtain the desired yield at milder operating conditions such as ambient temperature and atmospheric pressure was adopted in the CM of plant oils [39]. Despite the recommended reaction duration in the literature, it needs to reiterate that the reaction time required for the CM of plant oil would be dependent on the types of plant oils and catalysts used.

### 5. Conclusion

The present review evaluated the catalysts and operating conditions employed in the cross-metathesis of different types of plant oils, intending to pave a path for identifying the future research avenues in plant oil cross-metathesis. It was found that the plant oil with higher degree of unsaturation and longer unsaturated fatty acid chain length is the best raw material to be cross metathesized using a more preferable terminal olefin like 1-propene and 1-octene to avoid the formation of catalyst intermediate that could eventually decompose. Moreover, a more intensive research should be conducted to develop the stable and active heterogeneous ruthenium-based catalyst to allow simple catalyst separation and recovery. The existence of impurities in plant oil could lead to the CM that requires higher catalyst loading. Nevertheless, the catalyst concentration which is typically in ppm level should be optimised to avoid the undesired side reactions due to the excess of catalyst. Similarly, an intermediate reaction temperature of lower than 60°C is desirable to suppress side reactions. Under the optimum catalyst loading and reaction temperature, a more practical reaction time could then be identified to obtain a rationally high TON for the industrial application. To fill up the gap, the reaction kinetics and operating condition to cross-metathesise another potential feedstock, the palm oil, using 1-propene or 1-octene should be researched intensively to provide alternate route for value adding the palm oil.

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