



# Metathesis of unsaturated fatty acid esters derived from South African sunflower oil in the presence of a 3 wt.% $\text{Re}_2\text{O}_7/\text{SiO}_2\text{--Al}_2\text{O}_3/\text{SnBu}_4$ catalyst

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## Abstract

The metathesis of single- and multiple-component fatty acid ester systems derived from South African sunflower oil was investigated using a heterogeneous 3 wt.%  $\text{Re}_2\text{O}_7/\text{SiO}_2\text{--Al}_2\text{O}_3/\text{SnBu}_4$  catalyst system. A total conversion of the methyl ester of linoleic acid of 86.1% with a total diester yield of 20.4% was obtained. A total conversions of 76.2 and 72.2% with corresponding diester yields of 19.4 and 18.4%, respectively, were obtained in the cross-metathesis of (1) oleate/linoleate methyl esters and (2) a mixture of fatty acid esters derived from South African sunflower oil, respectively. Different reaction products showed varying sensitivity towards reaction temperature with dicarboxylic esters reaching a maximum yield at 60 °C. The 3 wt.%  $\text{Re}_2\text{O}_7/\text{SiO}_2\text{--Al}_2\text{O}_3/\text{SnBu}_4$  catalyst system reached maximum catalytic activity at 60 °C, but rapidly deactivated at higher reaction temperatures (80 °C).

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## 1. Introduction

The continuing increase in global demand for petroleum-based fuel and chemicals presents a challenge for chemists and engineers to exploit alternative resources to petroleum. Unsaturated fatty acid esters and fatty oils are attractive feedstocks for the production of a wide variety of intermediates and value-added products. Metathesis of unsaturated fatty acid esters results in the formation of simple

alkenes of different chain lengths and unsaturation as well as carboxylic esters with mono and dual functionalities [1]. Cross-metathesis of fatty oils and unsaturated fatty esters with alkenes allows the synthesis of short- and long-chain compounds which could, otherwise, be difficult to synthesize by other methods [2].

The metathetical transformation of unsaturated esters derived from sunflower oil (viz. alkyl oleates and linoleates) to intermediates for the synthesis of products with medical, cosmetic, polymeric and other applications, is of particular interest. For example, amongst other products produced upon metathesis of alkyl oleates and linoleates are unsaturated

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dicarboxylic esters, which are potential starting materials for the synthesis of polyesters, polyamides and macrocyclic compounds [1–4]. Ethenolysis (i.e. cross-metathesis with ethene) of methyl oleate, leads to the formation of methyl 9-decenoate, a potential starting material in the synthesis of many polymers and copolymers, for example, nylon-10 [2]. The metathesis of ethyl oleate results in the formation of 9-octadecene and diethyl 9-octadecene-1,18-dioate. The former can be dimerized and hydrogenated to give 10,11-dioctyleicosane, a lube-oil range hydrocarbon intermediate [5]. On the other hand, diethyl 9-octadecene-1,18-dioate can be converted to civetone, an odorant found in musk perfumes, by a combination of the Dieckmann condensation and a hydrolysis–decarboxylation reaction [6,7].

However, to commercialize the metathesis of functionalized alkenes, highly active, selective and stable catalysts are needed that can withstand deactivation from a broad range of organic functional groups. While previous work on the metathesis reaction of fatty esters derived from South African sunflower oil involved the homogeneous  $WCl_6/SnMe_4$  catalyst system [8], we report in this study results from the metathesis of single- and multiple-component fatty esters derived from South African sunflower oil using a 3 wt.%  $Re_2O_7/SiO_2-Al_2O_3/SnBu_4$  catalyst system. The heterogeneous  $Re_2O_7$  catalyst offers a number of advantages over the homogeneous W-based catalysts, namely, easy separation of the catalyst from the reaction mixture, regenerability of the catalyst and the fact that a  $Re_2O_7$  catalyst is already active at ambient reaction temperatures [2].

## 2. Experimental

### 2.1. Materials

Hexanes (Aldrich) were dried by refluxing over sodium metal and then stored under argon (Ar). Methyl linoleate (99.0%, Aldrich), methyl oleate (99.0%, Aldrich) and a mixture of fatty esters derived from South African sunflower oil (prepared in our laboratory) were purified from peroxides by allowing them to stand over calcined  $SiO_2-Al_2O_3$  (24.3%  $Al_2O_3$ , AKZO) under an argon atmosphere. Table 1 shows the composition of the ester mixture. Ammonium perrhenate ( $NH_4ReO_4$ , Fluka or Strem) and tetrabutyltin ( $SnBu_4$ , 93.0%, Aldrich) were used as purchased.

### 2.2. Apparatus

Reactions were carried out in a quartz glass reactor. The quartz-glass reactor (200 mm × 28 mm) was equipped with gas inlet, gas outlet, sample inlet and sample outlet tubes. Samples were introduced through the sample inlet tube under a stream of argon, at a flow rate of 7.0 cm<sup>3</sup>/min. Samples were collected with the aid of Ar pressure through the sample outlet tube.

### 2.3. Catalyst preparation

$SiO_2-Al_2O_3$  (particle size: 120–180 μm) was first dried at 120 °C. A 3 wt.%  $Re_2O_7/SiO_2-Al_2O_3$  catalyst was prepared by pore volume impregnation of  $SiO_2-Al_2O_3$  (0.97 g) with an aqueous solution of  $NH_4ReO_4$  (0.0332 g). The catalyst was placed in a quartz-glass reactor and dried at 120 °C in a mini-

Table 1  
Methyl esters derived from South African sunflower oil

Peak no.	m/e	Methyl ester (IUPAC name)	Common name	Abbreviations <sup>a</sup>	Mole (%)
1	270	Hexadecanoate	Palmitate	C <sub>17</sub> <sup>0</sup>	7.30
2	298	Octadecanoate	Stearate	C <sub>19</sub> <sup>0</sup>	6.00
3	296	<i>Cis</i> -9-Octadecanoate	Oleate	C <sub>19</sub> <sup>1</sup>	20.60
4	294	<i>Cis, cis</i> -9,12-Octadecanoate	Linoleate	C <sub>19</sub> <sup>2</sup>	65.10
5	326	Eicosanoate	Arachidate	C <sub>21</sub> <sup>0</sup>	0.30
6	354	Docosanoate	Behenate	C <sub>23</sub> <sup>0</sup>	0.70

<sup>a</sup> Superscript denotes the number of carbon–carbon double bonds, subscript denotes the number of carbon atoms. This applies throughout the text.

tube furnace followed by its calcination at 550 °C in a stream of air (7 cm<sup>3</sup>/min) for 3 h and subsequently under Ar, for 1 h.

## 2.4. Procedure

### 2.4.1. Metathesis of methyl linoleate

SnBu<sub>4</sub> (5.0 μl) was added to 2.0 cm<sup>3</sup> of hexane under a stream of argon. The SnBu<sub>4</sub> solution was added to 0.2 g of a calcined 3 wt.% Re<sub>2</sub>O<sub>7</sub>/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst (2.48 × 10<sup>-5</sup> mol Re) in a quartz-glass reactor and the mixture was stirred for 5 min followed by the addition of 9.0 cm<sup>3</sup> of hexane. Stirring was continued for about 2 min after which 0.5 cm<sup>3</sup> of methyl linoleate (1.5 × 10<sup>-3</sup> mol) was added. The reaction was allowed to stir for 3 h. The Sn:Re molar ratio of 0.6:1 was previously found by Sibeijn and Mol [9] to give optimum metathesis activity and has, therefore, been used throughout in this study.

### 2.4.2. Cross-metathesis of methyl oleate and methyl linoleate

An ester mixture (0.5 cm<sup>3</sup>) (0.375 cm<sup>3</sup> methyl linoleate/0.125 cm<sup>3</sup> methyl oleate) was metathesized in the presence of a 3 wt.% Re<sub>2</sub>O<sub>7</sub>/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst following the same procedure used above for the metathesis of methyl linoleate. The molar ratio of methyl linoleate to methyl oleate was about the same as that found in South African sunflower oil, viz. 3:1.

### 2.4.3. Metathesis of a mixture of fatty esters derived from South African sunflower oil

The ester mixture (0.5 cm<sup>3</sup>) (Table 1) was metathesized in the presence of a 3 wt.% Re<sub>2</sub>O<sub>7</sub>/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>

catalyst following the same procedure used above for the metathesis of methyl linoleate.

## 2.5. Analysis

GC analyses were performed on a Carlo Erba 6000 Vega series 3 GC equipped with a cold on-column injector, a DB-1 fused silica capillary column (15 m × 0.538 mm, maximum temperature 340 °C, J&W Scientific) and FID using the following conditions: carrier gas (He), detector temperature (300 °C), oven programmed from 100 to 150 °C at 10 °C/min, 150–160 °C at 1 °C/min, 160–280 °C at 15 °C/min. The substrate conversions were calculated from the peak areas of the GC analyses corrected for the molecular response by Ackman's method [10]:

$$\% \text{ Conversion} = 1 - \frac{C_s}{\sum C_i}$$

where  $i = 1, 2, \dots, \xi$ ;  $C_s$  is the corrected peak area for the substrate ester;  $C_i$  denotes the corrected peak area for the component  $i$  in the product mixture with  $\xi$  components.

## 3. Results and discussion

### 3.1. Metathesis of methyl linoleate

#### 3.1.1. Reaction products

Table 2 shows the products obtained upon metathesis of methyl linoleate in the presence of a 3 wt.% Re<sub>2</sub>O<sub>7</sub>/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>/SnBu<sub>4</sub> catalyst. The substrate conversion of 86.1% was attained in 2 h reaction time with a selectivity of >95% towards primary metathesis products:

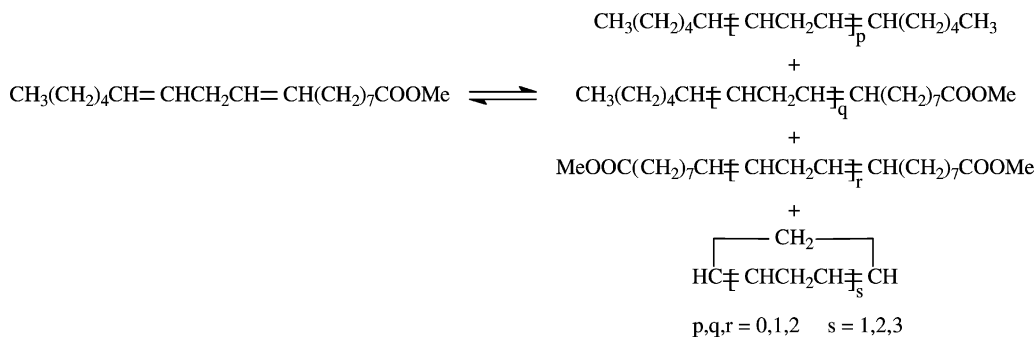


Table 2

Products resulting from the metathesis of methyl linoleate at 20 °C after 2 h reaction time in the presence of a 3 wt.%  $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3/\text{SnBu}_4$  catalyst system

Carbon no.	Product	Carbon skeleton	m/e	Yield (%)
<b>Simple alkenes</b>				
$\text{C}_{12}^1$	6-Dodecene	$\text{C}_6=\text{C}_6$	168	13.9
$\text{C}_{15}^2$	6,9-Pentadecadiene	$\text{C}_6=\text{C}_3=\text{C}_6$	208	8.9
$\text{C}_{18}^3$	6,9,12-Octadecatriene	$\text{C}_6=(\text{C}_3)_2=\text{C}_6$	248	3.7
$\text{C}_{21}^4$	6,9,12,15-Heneicosatetraene	$\text{C}_6=(\text{C}_3)_3=\text{C}_6$	288	1.1
$\text{C}_{24}^5$	6,9,12,15,18-Tetracosapentaene	$\text{C}_6=(\text{C}_3)_4=\text{C}_6$	352	0.5
<b>Monoesters</b>				
$\text{C}_{16}^1$	Methyl 9-pentadecenoate	$\text{C}_6=\text{C}_8\text{COOC}$	254	31.0
$\text{C}_{19}^2$	Methyl 9,12-octadecadienoate	$\text{C}_6=\text{C}_3=\text{C}_8\text{COOC}^*$	294	13.9
$\text{C}_{22}^3$	Methyl 9,12,15-heneicosatrienoate	$\text{C}_6=(\text{C}_3)_2=\text{C}_8\text{COOC}$	334	5.4
$\text{C}_{25}^4$	Methyl 9,12,15,18-tetracosatetraenoate	$\text{C}_6=(\text{C}_3)_3=\text{C}_8\text{COOC}$	375	0.8
$\text{C}_{28}^5$	Methyl 9,12,15,18,21-heptacosapentaenoate	$\text{C}_6=(\text{C}_3)_4=\text{C}_8\text{COOC}$	413	0.4
<b>Diesters</b>				
$\text{C}_{20}^1$	Dimethyl 9-octadecenedioate	$\text{COOCC}_8=\text{C}_8\text{COOC}$	340	12.9
$\text{C}_{23}^2$	Dimethyl 9,12-heneicosadienedioate	$\text{COOCC}_8=\text{C}_3=\text{C}_8\text{COOC}$	380	5.1
$\text{C}_{26}^3$	Dimethyl 9,12,15-tetracosatrienedioate	$\text{COOCC}_8=(\text{C}_3)_2=\text{C}_8\text{COOC}$	421	1.8
$\text{C}_{29}^4$	Dimethyl 9,12,15,18-heptacosatetraenedioate	$\text{COOCC}_8=(\text{C}_3)_3=\text{C}_8\text{COOC}$	–	0.6

Substrate:Re:SnBu<sub>4</sub> = 60:1:0.6.

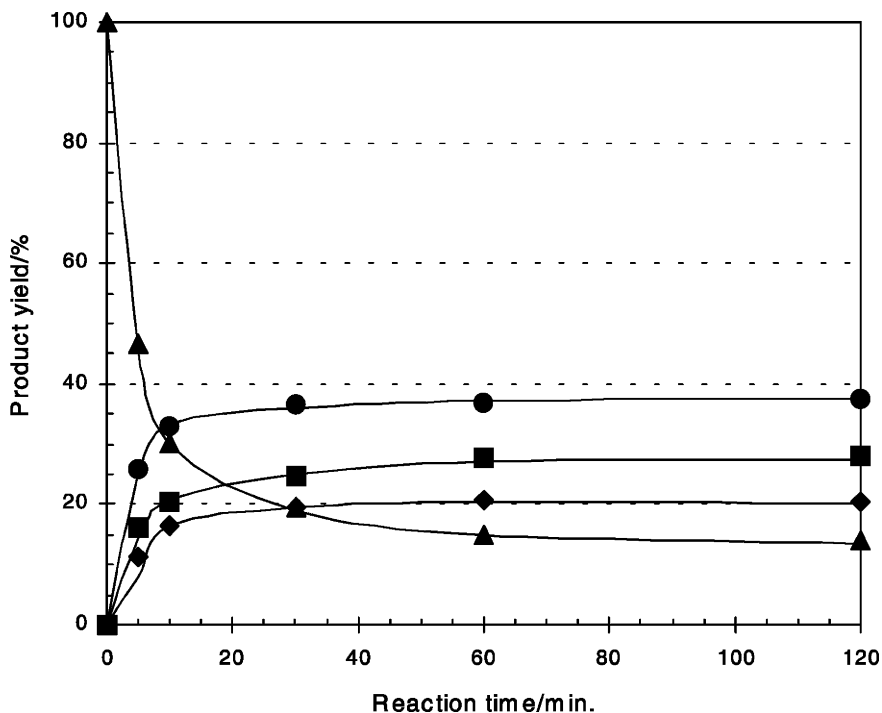


Fig. 1. The yield of linear alkenes, monoesters and diesters as a function of reaction time resulting from the metathesis of methyl linoleate in the presence of the 3 wt.%  $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3/\text{SnBu}_4$  catalyst system at 20 °C. ●, monoesters; ■, simple alkenes; ◆, diesters; ▲, methyl linoleate.

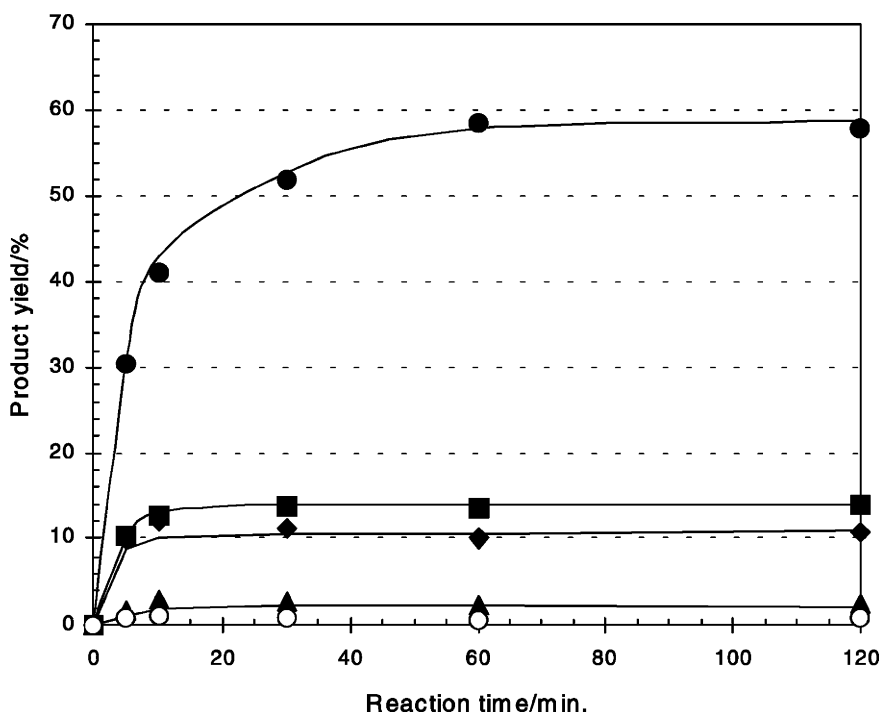


Fig. 2. The yield of monoenes, dienes, trienes, tetraenes and pentaenes as a function of reaction time resulting from the metathesis of methyl linoleate in the presence of a 3 wt.%  $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3/\text{SnBu}_4$  catalyst system. Reaction temperature, 20 °C. ●, monoenes; ■, dienes; ◆, trienes; ▲, tetraenes; ○, pentaenes.

Fig. 1 shows the yields of linear compounds, viz. simple alkenes, monoesters and diesters as a function of reaction time. Fig. 2 shows the yields for monoenes, dienes, trienes, tetraenes and pentaenes as a function of reaction time.

From the results (Table 2), it is clear that a 3 wt.%  $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3/\text{SnBu}_4$  catalyst system is highly active and selective in the metathesis of polyunsaturated fatty esters. Indeed, the metathesis activity of a 3 wt.%  $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3/\text{SnBu}_4$  catalyst system for methyl linoleate is comparably higher (linoleate conversion of 86.1%) than that reported in the literature for the classical homogeneous  $\text{WCl}_6/\text{SnMe}_4$  catalytic system (linoleate conversion of 84%) [11,12]. The 3 wt.%  $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3/\text{SnBu}_4$  catalytic system is also very selective towards primary metathesis products (> 95%). Secondary metathesis products were not observed, implying that side reactions, for example, isomerization and oligomerization, were absent. This high selectivity might not only be due to the low reaction temperature, but also to complexation of

the ester group to the Brønsted acid sites on the support, preventing side reactions such as double bond shift. Previous reports have indicated that secondary metathesis products do form when normal olefins are metathesized with a  $\text{Re}_2\text{O}_7$  catalyst supported on the highly acidic  $\text{SiO}_2\text{-Al}_2\text{O}_3$  support [13,14].

### 3.1.2. The influence of substrate purity

Methyl linoleate, like most unsaturated fatty acid esters, is prone to an oxidation reaction, although its oxidation is slower than that of linoleic acid [15]. The initial products of peroxidation are hydroperoxides (ROOH), which subsequently decompose to form a wide range of secondary products including epoxides, aldehydes, ketones, etc. Both peroxides and secondary oxidation products are known to poison supported  $\text{Re}_2\text{O}_7$  and  $\text{MoO}_3$  metathesis catalysts [16].

In this study the influence of substrate purity, expressed in terms of peroxide value, on the reaction of methyl linoleate and the product distribution was investigated. Two samples of methyl linoleate, with

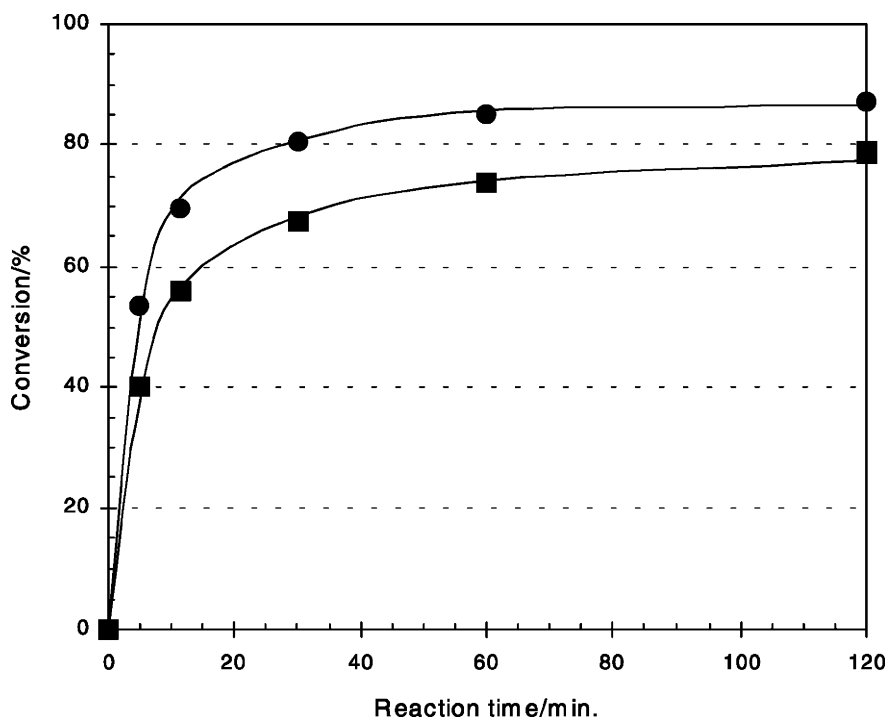


Fig. 3. The influence of peroxides on the reactivity of methyl linoleate in the presence of a 3 wt.%  $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3/\text{SnBu}_4$  catalytic system. Substrate:Re:SnBu<sub>4</sub> molar ratio = 60:1:0.6. ●, peroxide value <1 mg/dm<sup>3</sup>; ■, peroxide value = 3–10 mg/dm<sup>3</sup>.

the first sample having peroxide value of <1 mg/dm<sup>3</sup> and the second sample registering a peroxide value of 3–10 mg/dm<sup>3</sup>, were metathesized in the presence of a 3 wt.%  $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3/\text{SnBu}_4$  catalyst system. Fig. 3 compares the metathesis reactivities of the two samples of methyl linoleate, while Table 3 compares the product yields obtained for the two linoleate samples.

From the results in Fig. 3 it can be seen that indeed the presence of peroxides has an adverse effect

Table 3

Products resulting from metathesis of pure and oxidized samples of methyl linoleate in the presence of a 3 wt.%  $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3/\text{SnBu}_4$  catalyst system

Peroxide value (mg/l)	Yield (%)			
	Alkenes	Monoesters	Dieters	Total metathesis
<1	28.1	37.6	20.4	86.1
3–10	24.0	38.8	16.3	79.1

Reaction time, 2 h; substrate:Re:SnBu<sub>4</sub> = 60:1:0.6.

on the metathesis activity of the  $\text{Re}_2\text{O}_7$  catalyst. This further support the findings previously made by Sibeijn [16] using methyl oleate, a mono-unsaturated ester. The electron-rich peroxides possibly poison the  $\text{Re}_2\text{O}_7$  catalyst by coordination to the catalytic active site. Purification of the methyl linoleate prior to the metathesis reaction resulted in improved product yields, especially for dicarboxylic esters.

### 3.1.3. The influence of reaction temperature

The metathesis activity and selectivity of a 3 wt.%  $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3/\text{SnBu}_4$  catalyst system was investigated at different reaction temperatures with methyl linoleate as the substrate ester. Fig. 4 shows the conversion of methyl linoleate with time at different reaction temperatures. Maximum metathesis activity was attained at 20–60 °C with methyl linoleate conversion increasing from 86.1 to 86.9%. These results are in agreement with those obtained for methyl oleate [2]. At elevated reaction temperatures (80–100 °C) lower substrate conversions were obtained. A similar

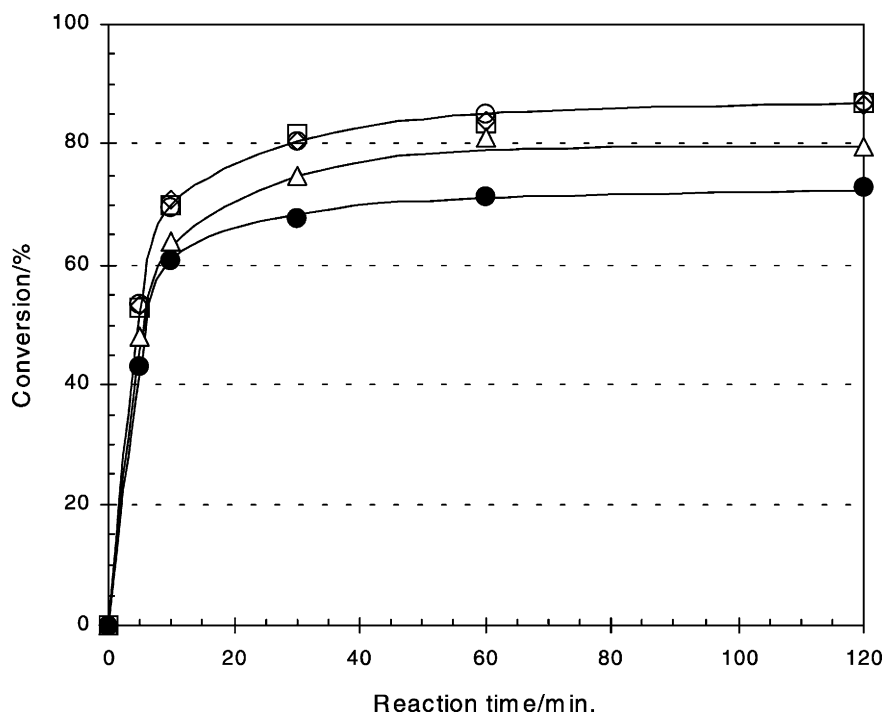
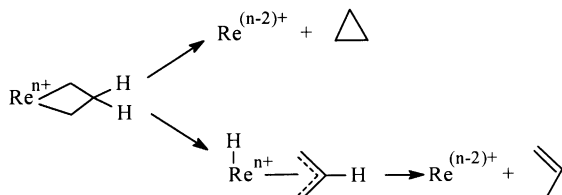


Fig. 4. The influence of reaction temperature on the activity of a 3 wt.%  $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3/\text{SnBu}_4$ /methyl linoleate catalytic system. Substrate:Re:SnBu<sub>4</sub> molar ratio = 60:1:0.6. ○, 20 °C; □, 40 °C; ◇, 60 °C; △, 80 °C; ●, 100 °C.

temperature-dependent deactivation pattern was also obtained by Spronk et al. [17] for propene metathesis in the presence of a 12 wt.%  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3/\text{SnEt}_4$  catalyst system. They proposed an intrinsic deactivation mechanism as the main cause of deactivation, viz. a temperature-dependent reductive elimination of the metallacyclobutane complex which is the intermediate in the metathesis reaction: In a reductive



elimination of the metallacyclobutane intermediate, two routes are possible, viz. the formation of cyclopropane or  $\beta$ -elimination to an alkene. The above deactivation mechanism seems highly probable under our reaction conditions, and would account for the deactivation of a 3 wt.%  $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3/\text{SnBu}_4$

catalyst system. However, since coke formation at temperatures as low as 30 °C is also possible [18], diffusion constraints resulting from site covering and pore-mouth plugging cannot be completely overruled. Finally, a Wittig-type reaction between the carbonyl group of the ester and the rhenium carbene might also be responsible for a decrease in catalytic activity [2]. However, it is well known that this catalyst

Table 4

Optimum reaction temperatures for maximum yields of various products upon metathesis of methyl linoleate in the presence of a 3 wt.%  $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3/\text{SnBu}_4$  catalyst system

Product	$T$ (°C)
Simple alkenes	20–60
Monoesters	40–60
Diesters	60
Monoenes	20–40
Dienes	20–40
Trienes	20–40
Tetraenes	40

Reaction time, 2 h; substrate:Re:SnBu<sub>4</sub> = 60:1:0.6.

Table 5

Products resulting from a cometathesis of methyl linoleate and methyl oleate in the presence of a 3 wt.%  $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3/\text{SnBu}_4$  catalyst system at 20 °C

Carbon no.	Product	Carbon skeleton	Yield (%)
<b>Simple alkenes</b>			
$\text{C}_{12}^1$	6-Dodecene	$\text{C}_6=\text{C}_6$	5.9
$\text{C}_{15}^2$	6,9-Pentadecadiene	$\text{C}_6=\text{C}_3=\text{C}_6$	10.4
$\text{C}_{18}^3$	6,9,12-Octadecatriene	$\text{C}_6=(\text{C}_3)_2=\text{C}_6$	6.7
$\text{C}_{21}^4$	6,9,12,15-Heneicosatetraene	$\text{C}_6=(\text{C}_3)_3=\text{C}_6$	0.4
$\text{C}_{24}^5$	6,9,12,15,18-Tetracosapentaene	$\text{C}_6=(\text{C}_3)_4=\text{C}_6$	–
<b>Monoesters</b>			
$\text{C}_{16}^1$	Methyl 9-pentadecenoate	$\text{C}_6=\text{C}_8\text{COOC}$	21.9
$\text{C}_{19}^1$	Methyl 9-octadecenoate	$\text{C}_9=\text{C}_8\text{COOC}$	13.1
$\text{C}_{19}^2$	Methyl 9,12-octadecadienoate	$\text{C}_6=\text{C}_3=\text{C}_8\text{COOC}$	10.8
$\text{C}_{22}^3$	Methyl 9,12,15-heneicosatrienoate	$\text{C}_6=(\text{C}_3)_2=\text{C}_8\text{COOC}$	8.5
$\text{C}_{25}^4$	Methyl 9,12,15,18-tetracosatetraenoate	$\text{C}_6=(\text{C}_3)_3=\text{C}_8\text{COOC}$	2.5
$\text{C}_{28}^5$	Methyl 9,12,15,18,21-heptacosapentaenoate	$\text{C}_6=(\text{C}_3)_4=\text{C}_8\text{COOC}$	0.5
<b>Diesters</b>			
$\text{C}_{20}^1$	Dimethyl 9-octadecenedioate	$\text{COOCC}_8=\text{C}_8\text{COOC}$	12.9
$\text{C}_{23}^2$	Dimethyl 9,12-heneicosadienedioate	$\text{COOCC}_8=\text{C}_3=\text{C}_8\text{COOC}$	4.6
$\text{C}_{26}^3$	Dimethyl-9,12,15-tetracosatrienedioate	$\text{COOCC}_8=(\text{C}_3)_2=\text{C}_8\text{COOC}$	1.5
$\text{C}_{29}^4$	Dimethyl-9,12,15,18-heptacosatetraenedioate	$\text{COOCC}_8=(\text{C}_3)_3=\text{C}_8\text{COOC}$	0.4

Re:SnBu<sub>4</sub> = 1:0.6; reaction time, 3 h.

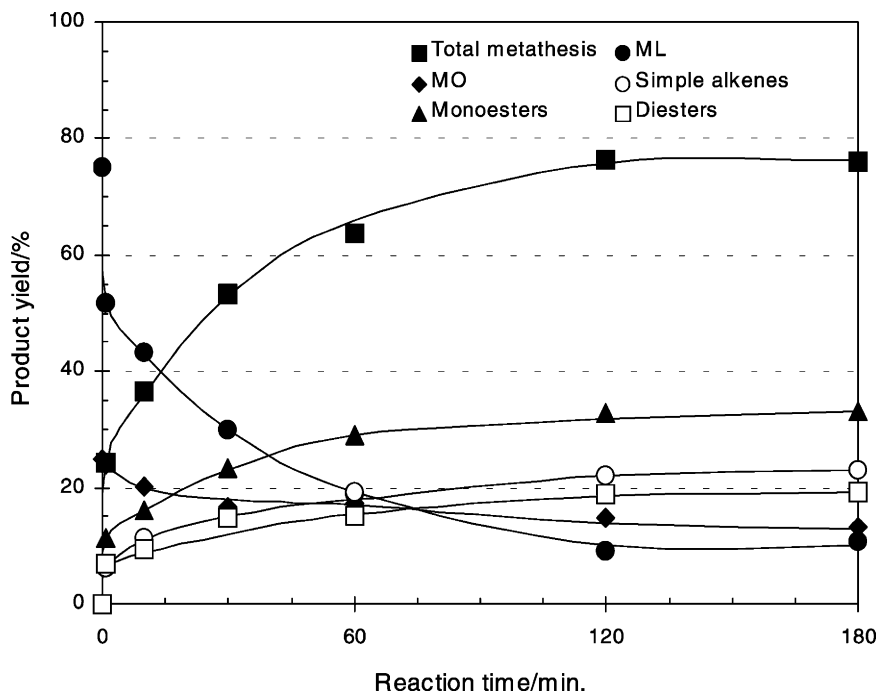


Fig. 5. Products obtained from cometathesis of methyl oleate (MO) and methyl linoleate (ML) in the presence of a 3 wt.%  $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3/\text{SnBu}_4$  catalyst system at 20 °C.



can be regenerated via calcination at 550 °C, followed by further addition of promoter [2,4].

High reaction temperatures also affected the yields of various reaction products. The optimum reaction temperatures for maximum yields of various reaction products are presented in Table 4. For the production of dicarboxylic esters, for example, the optimum reaction temperature was 60 °C.

### 3.2. Cross-metathesis of methyl oleate and methyl linoleate

Table 5 presents the yields of products obtained from the cross-metathesis reaction of oleate and linoleate methyl esters in the presence of a 3 wt.%  $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3/\text{SnBu}_4$  catalyst system at 20 °C. Equilibrium was attained in 3 h with conversions of 85.6 and 47.6% for methyl linoleate and methyl oleate, respectively. Fig. 5 presents the yields of alkenes, monoesters and diesters with time while Fig. 6 presents the yields of monoenes, dienes, trienes, tetraenes and pentaenes with reaction time. The selectivity towards primary metathesis products was >95%.

Table 6

Products resulting from the metathesis of a mixture of fatty esters derived from South African sunflower oil in the presence of a 3 wt.%  $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3/\text{SnBu}_4$  catalyst system at 20 °C

Carbon no.	Carbon skeleton	Yield (%)
Simple alkenes		
$\text{C}_{12}^1$	$\text{C}_6=\text{C}_6$	10.7
$\text{C}_{15}^2$	$\text{C}_6=\text{C}_3=\text{C}_6$	10.0
$\text{C}_{18}^3$	$\text{C}_6=(\text{C}_3)_2=\text{C}_6$	5.2
$\text{C}_{21}^4$	$\text{C}_6=(\text{C}_3)_3=\text{C}_6$	0.1
$\text{C}_{21}^4\text{C}_{24}^5$	$\text{C}_6=(\text{C}_3)_4=\text{C}_6$	–
Monoesters		
$\text{C}_{16}^1$	$\text{C}_6=\text{C}_8\text{COOC}$	20.1
$\text{C}_{19}^1$	$\text{C}_9=\text{C}_8\text{COOC}$	13.8
$\text{C}_{19}^2$	$\text{C}_6=\text{C}_3=\text{C}_8\text{COOC}$	14.0
$\text{C}_{22}^3$	$\text{C}_6=(\text{C}_3)_2=\text{C}_8\text{COOC}$	5.6
$\text{C}_{25}^4$	$\text{C}_6=(\text{C}_3)_3=\text{C}_8\text{COOC}$	2.1
$\text{C}_{28}^5$	$\text{C}_6=(\text{C}_3)_4=\text{C}_8\text{COOC}$	–
Diesters		
$\text{C}_{20}^1$	$\text{COOCC}_8=\text{C}_8\text{COOC}$	11.9
$\text{C}_{23}^2$	$\text{COOCC}_8=\text{C}_3=\text{C}_8\text{COOC}$	5.0
$\text{C}_{26}^3$	$\text{COOCC}_8=(\text{C}_3)_2=\text{C}_8\text{COOC}$	1.2
$\text{C}_{29}^4$	$\text{COOCC}_8=(\text{C}_3)_3=\text{C}_8\text{COOC}$	0.3

Re:SnBu<sub>4</sub> = 1:0.6; reaction time, 3 h.

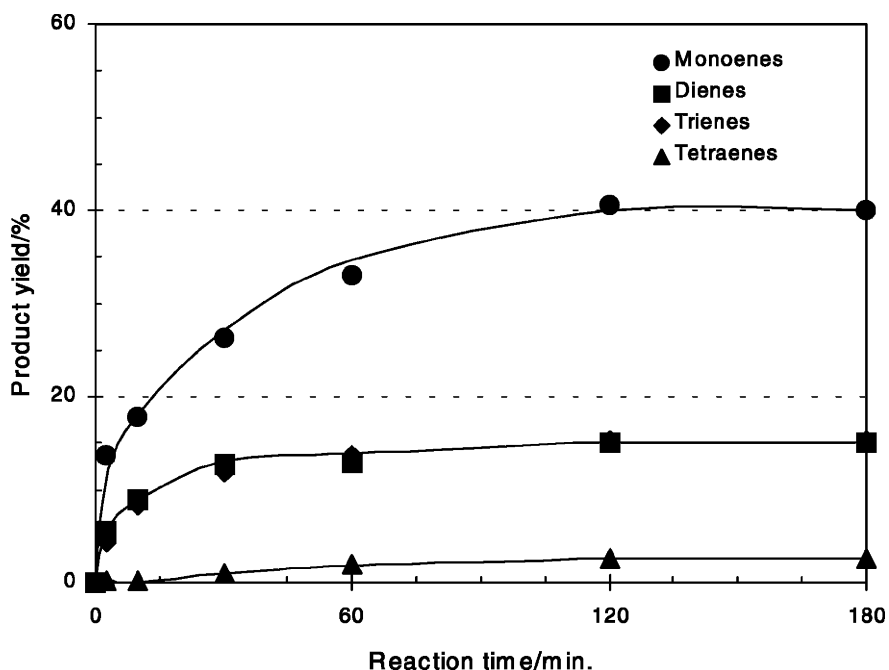


Fig. 6. Monoenes, dienes and higher polyenes resulting from the cometathesis reaction of methyl linoleate and methyl oleate in the presence of a 3 wt.%  $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3/\text{SnBu}_4$  catalyst system at 20 °C.

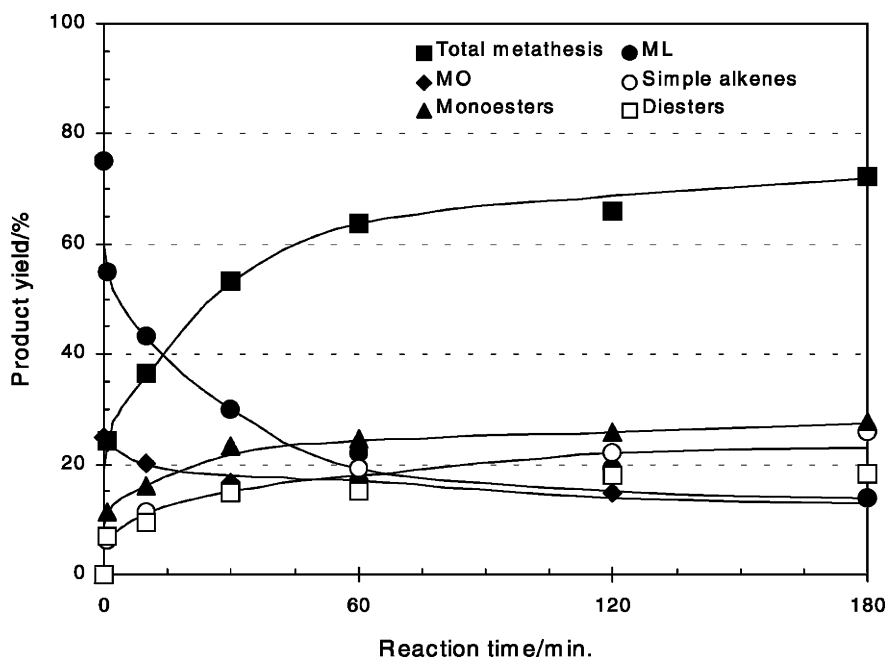


Fig. 7. Products obtained from the metathesis of a mixture of fatty acid esters in the presence of a 3 wt.%  $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3/\text{SnBu}_4$  catalytic system at 20 °C.

From the results in Table 5 it can be seen that the reactivity of the diene-ester was about twice that of a mono-ester. The higher reactivity of the linoleic ester compared to oleic ester is clearly a direct consequence of the presence of two carbon-carbon double bonds in the diene-ester as opposed to only one in the mono-ester. The equilibrium ratio of alkenes:monoesters: diesters was approximately 1:2:1, about the same ratio as that obtained in the self-metathesis reaction of methyl linoleate.

### 3.3. Metathesis of a mixture of fatty esters derived from South African sunflower oil

Nicolaides et al. [8] previously reported on the homogeneously metathesized mixture of fatty acid esters derived from sunflower oil using the  $\text{WCl}_6/\text{SnMe}_4$  catalytic system. We now report on the heterogeneously metathesized mixture of fatty acid esters derived from South African sunflower oil using a 3 wt.%  $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3/\text{SnBu}_4$  catalytic system. The metathesis products resulting from the metathesis of a mixture of fatty esters are shown in Table 6. The

time-dependent yields of substrates and metathesis products are presented in Fig. 7. Within 1 h reaction time, 72.0% linoleate and 30.0% oleate had reacted. After 3 h reaction time, the conversions were 81.0 and 45.0% for linoleate and oleate esters, respectively. The selectivity towards primary metathesis products was >95%. The yields obtained for simple alkenes, monoesters and diesters were 26.0, 27.8 and 18.4%, respectively, representing a slight deviation from the product ratio obtained in single- and double-component fatty ester systems discussed earlier. The yields of monoenes, dienes and higher polyenes as a function of reaction time are presented in Fig. 8.

The activity of the  $\text{Re}_2\text{O}_7$  was, however, lower in the case of a multiple-ester mixture derived from sunflower oil as opposed to a two-component oleic/linoleic ester mixture. The low metathesis activity in the former mixture could possibly be due to catalyst poisoning resulting from a side reaction between polar ester groups on “spectator” saturated fatty acid esters and the catalytic active site; a Wittig-type reaction [2].

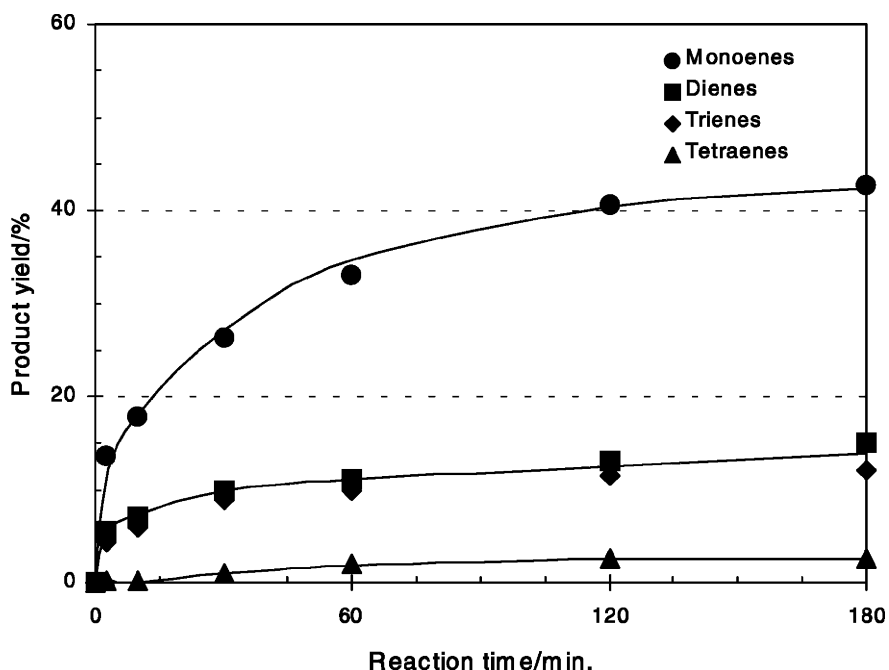


Fig. 8. The yield of monoenes, dienes, trienes and tetraenes resulting from the metathesis of a mixture of fatty acid esters derived from sunflower oil in the presence of a 3 wt.%  $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3/\text{SnBu}_4$  catalyst system.

#### 4. Conclusions

Single and multiple-component fatty acid esters derived from South African sunflower oil easily undergo metathesis in the presence of a heterogeneous 3 wt.%  $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3/\text{SnBu}_4$  catalyst system yielding high substrate conversions and a selectivity >95%. At 20 °C the product yields are compared to those obtained with the classical homogeneous  $\text{WCl}_6/\text{SnMe}_4$  catalyst system. The absence of secondary metathesis products serves as evidence that double bond migration does not occur under the given reaction conditions. Furthermore, different reaction products show varying sensitivities towards reaction temperature with the result that maximum yields of specific products can be obtained upon careful selection of the reactor temperature; for example, dicarboxylic esters reach maximum yield at 60 °C. Although a slight increase in metathesis activity of a 3 wt.%  $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3/\text{SnBu}_4$  catalyst system is observed at 60 °C, a rapid decrease in metathesis activity occurs at higher reaction temperatures (>80 °C) due to the possible reduction of the metallacyclobutane

intermediate and from the pore-mouth plugging on  $\text{SiO}_2\text{-Al}_2\text{O}_3$  support resulting from coke deposition. For a multiple-component fatty ester mixture derived from sunflower oil, deactivation of the  $\text{Re}_2\text{O}_7$  catalyst may also result from a possible side reaction between polar ester groups on “spectator” saturated esters with the catalytic active site; a Wittig-type reaction [2].

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