Co-Metathesis Reaction of Crude Palm Oil and Ethene

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ABSTRACT: The co-metathesis reaction of crude palm oil with ethene in the presence of WCL_6/Me_4Sn, followed by termination of this reaction with methanol, gives terminal alkenes. The major metathesis products are 1-decene and methyl 9-decenoate.

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KEY WORDS: Co-metathesis, ethene, palm oil.

Vegetable oil, such as palm oil, is an important world commodity (1,2). Therefore, further studies on the reactivity of this oil are imperative and have been an important subject for the extension of its usages. This is especially so as Malaysia, being the world's largest palm oil exporter, is able to produce this commodity in abundance and at a competitive price with other vegetable oils. Recently, we reported that the self-metathesis of RHA (rice husk ash)-treated Malaysian crude palm oil (CPO) with a WCl_6/Me_4Sn catalyst system gave mainly linear alkenes (9-octadecene and 6-pentadecene) and alkyl esters (methyl palmitate and methyl oleate) when the reaction was quenched with methanol (3,4). This communication reports our first successful co-metathesis reaction of RHA-treated CPO and ethene.

EXPERIMENTAL PROCEDURES

All manipulations of solvents, catalysts, and co-catalyst were carried out as described earlier (3). Tungsten hexachloride (WCl_6) was purified by sublimation before use. Tetramethyltin (Me_4Sn) was purchased from Aldrich (Aldrich, Gillingham, United Kingdom), and the CPO was obtained from the Palm Oil Research Institute of Malaysia (Bangi, Selangor, Malaysia). The metathesis reaction was carried out at 30°C for 24 h in dry chlorobenzene by using a typical homogenous catalyst, WCl_6/Me_4Sn. The ratio of WCl_6 to CPO was 1:10 (by weight), and the molar ratio of Me_4Sn to WCl_6 was 2:1. Ethene was applied immediately after the addition of the catalysts to the CPO solutions, and the ethene pressure was maintained at 14 psi for 24 h. The reaction was then terminated with methanol, and the products were analyzed by gas chromatography/mass spectroscopy with a Hewlett Packard (Palo Alto, CA) HP5890A series II/HP5970 with a Quadrex capillary column.

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RESULTS AND DISCUSSION

The important compounds produced, based on the peak areas, are shown in Table 1. Figure 1 shows the gas chromatogram of these products. Interestingly, the methanol-terminated co-metathesis reaction gives a rather simple product distribution. It gives mainly 1-decene and 9-decenoate, together with small amounts of other terminal alkenes (Table 1). Methyl palmitate and methyl oleate are also formed by transesterification with methanol at a good yield but are not metathesis products (3,4).

As expected, the co-metathesis of CPO (a mixture of triglycerides of oleic, linoleic, and palmitic acids) with ethene gives a mixture of 1-heptene, 1,4-decadiene, and 1-decene (Scheme 1). The methyl esters are formed by the catalytic transesterification of triglycerides with methanol in the product mixture (4). 9-Octadecene is considered to be formed by the self-metathesis of the triglycerides (3,4). Methyl linoleate is not observed in the final product; thus the metathesis of the linoleate was nearly complete.

The above results open another useful tool for synthesizing various chemical products, including useful unsaturated esters and terminal alkenes, from CPO. Terminal alkenes, especially 1-decene, have been reported as important intermediates for the synthesis of oligomers and lubricants (5–10).

TABLE 1
Products of the Co-Metathesis of Crude Palm Oil and Ethene After Termination with Methanol

Peak number	Compounds	% Yields
1	1-Heptene	0.62
2	1-Decene	18.90
3	1,4-Decadiene	0.37
4	Methyl 9-decenoate	17.50
5	9-Octadecene[a]	2.08
6	Methyl palmitate[b]	49.45
7	Methyl oleate[b]	11.38

[a]By self-metathesis
[b]Nonmetathesis products.

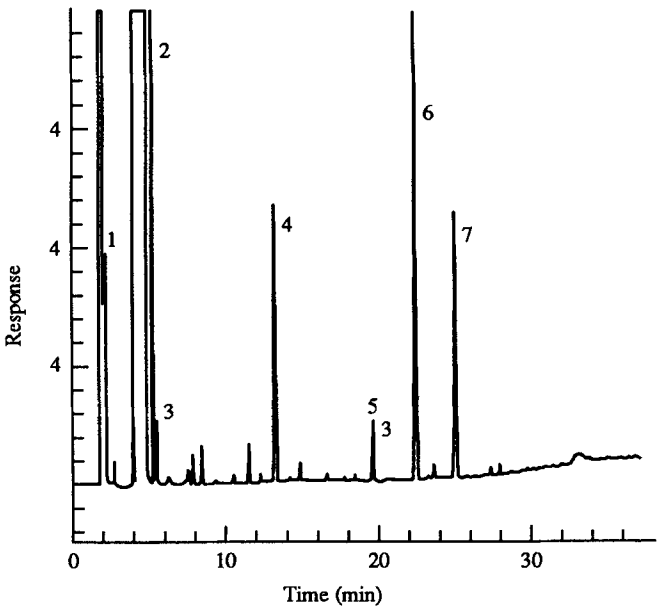
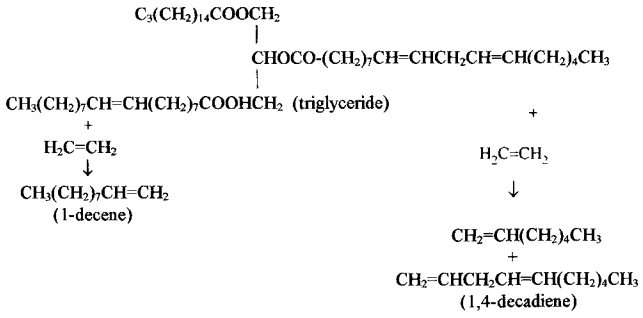


FIG. 1. Gas chromatogram of co-metathesis products: 1, 1-heptene; 2, 1-decene; 3, 1,4-decadiene; 4, methyl 9-decenoate; 5, 9-octadecene; 6, methyl palmitate; and 7, methyl oleate.



SCHEME 1

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