Final Technical Report

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Executive Summary

The US chemical industry is $460 billion in size where a $150 billion segment of which is non-oxygenated chemicals that is sourced today via petroleum but is addressable by a renewable feedstock if one considers a more chemically reduced feedstock such as vegetable oils. Vegetable oil, due to its chemical functionality, provides a largely untapped opportunity as a renewable chemical source to replace petroleum-derived chemicals and produce platform chemicals unavailable today. This project examined the fertile intersection between the rich building blocks provided by vegetable oils and the enhanced chemical modification capability provided by metathesis chemistry. The technology advanced in this study is the process of ethylene cross-metathesis (referred to as ethenolysis) with vegetable oil and vegetable oil derivatives to manufacture the platform-chemical 9-decenoic acid (or 9DA) and olefin co-products.

The project team meet its goals of demonstrating improved catalyst efficiencies of several multiples, deepening the mechanistic understanding of metathesis, synthesis and screening of dozens of new catalysts, designing and modeling commercial processes, and estimating production costs. One demonstrable result of the study was a step change improvement in catalyst turnover number in the ethenolysis of methyl oleate as reported here. We met our key measurable of producing 100 lbs of 9DA at the pilot-scale, which demonstrated ability to scale-up ethenolysis.

DOE Project funding had significant positive impact on development of metathetically modified vegetable oils more broadly as the Cargill/Materia partnership, that was able to initiate primarily due to DOE funding, has succeeded in commercializing products, validating metathesis as a platform technology, and expanding a diverse products portfolio in high value and in large volume markets. Opportunities have expanded and business development has gained considerable momentum and enabled further expansion of the Materia/Cargill relationship. This project exceeded expectations and is having immediate impact on DOE success by replacing petroleum products with renewables in a large volume application today.

Background

Vegetable oil, due to its chemical functionality, provides yet untapped opportunity as a renewable chemical source to replace petroleum-derived chemicals and produce platform chemicals unavailable today. The oilseed biorefinery proposed here is versatile in application to the domestically produced oils including soybean, corn, canola, sunflower, peanut, linseed, and cottonseed, as well as in integration with existing biorefinery concepts. Corn oil is converted to platform chemicals in a biorefinery along side starch conversion to ethanol. Similarly, soybean and other oils are processed into a similar distribution of platform chemicals with biodiesel in a biorefinery product mix. A stand-alone biorefinery converting vegetable oil into platform chemicals is also envisioned. Keys to the success of this biorefinery concept are the development of cost effective chemical conversion technologies in concert with product applications and market development.

The attributes of the industrial petrochemical refinery have been extended in recent years to the "biorefinery" concept. A biorefinery shares many features with the petrochemical refinery, including a diverse production platform for fuels and commodity chemicals, yet differs significantly in the use of renewable feedstocks and the associated economic and environmental benefits. Such benefits include smaller environmental footprints, more attractive life cycle analyses and the strengthening of the rural economy through the diversified use of biomass feedstocks.

A foundation of the biorefinery concept is the development of novel platform intermediates. Many platform intermediates are being developed commercially, including succinic acid, lactic acid and 3-hydroxypropionic acid. Common features of these programs are that they are derived from carbohydrate or biomass sugars using biotechnological processes. Carbohydrates, however, are oxygenated molecules. This limits the scope of the products that can be made, especially when one considers that most biological processes further oxidize the substrate. Thus, approximately $70 billion of the $460 billion, or less than 15% of the US chemical industry, is addressable by fermentation of carbohydrates. A larger, $150 billion segment of non-oxygenated chemicals is addressable if one considers a more chemically reduced feedstock, similar to petroleum. One such feedstock is vegetable oil.

Remarkably, the biorefinery concept has not been fully explored for the production of fuels and chemicals from vegetable oils, despite the fact that world production exceeds 90 million metric tons per year. One possible reason is the historical lack of tools for the chemical modification of vegetable oils. The recent development of novel catalysts, both biological and chemical, enable chemistries that previously have been difficult and uneconomical.

Project Objective

Develop a novel platform of industrial chemicals based on innovative applications of metathesis chemistry that will serve as the foundation of an oilseed biorefinery.

A multi-disciplinary team collaborated in the development of the 9-decenoic acid chemical platform produced by the ethylene cross-metathesis, or so-called ethenolysis reaction, of vegetable oils and vegetable oil derivatives. The team applied catalyst technology, catalyst synthesis, process design, and scale-up, and applications. Cargill partnered with Materia, Inc. to develop and screen catalysts and to develop process flowsheets, simulations, and economic estimates for the metathesis chemistry. Materia and other Cargill partners expanded the concept by developing novel commercial applications of the chemicals derived from this platform. The task breakdown follows.

Task 1: Demonstrate the feasibility of a biocatalytic process for the modification of the lipid feedstock.
Task 2: Identify and optimize metathesis catalysts and associated processes as applied to unsaturated fatty acids and products derived there from.
Task 3: Identify enabling chemistries for the modification of metathetical derivatives and application of these products.
Task 4: Integration of the steps above with the broader concept of the oilseed biorefinery through developing separation schemes, detailed processes modeling, and economic modeling.

Tasks 1 and 3 were not pursued and Task 4 was significantly reduced in scope due to funding reduction to the DOE and refocusing of project priorities on metathesis chemistry development. Technical summaries of Tasks 2 and 4 follow.

Technical Summary of Task 2

Introduction

Olefin metathesis is a fundamental chemical reaction involving the rearrangement of carbon-carbon double bonds. This reaction can be used to couple, cleave, ring-close, ring-open, or polymerize olefinic molecules. The olefin metathesis cleavage (ethenolysis, i.e., cross-metathesis with ethylene) of unsaturated vegetable oil is the key enabling step of the proposed oilseed refinery. Although the interest in applying olefin metathesis technology to the production of value-added chemicals from natural oils has been long-standing, early work with traditional molybdenum, tungsten, and rhenium catalysts showed them to be too chemically sensitive to be commercially useful with the highly functional natural oils. After the invention of highly-active, but chemically-tolerant, ruthenium metathesis catalysts by Grubbs in the mid-1990's, several academic researchers including Grubbs,[1] Mol,[2] Larock[3] and Warvel[4] as well as researchers at Dow Chemicals[5] had demonstrated greatly improved reactivity with highly purified oils, suggesting that these new catalysts have great promise for biomass conversion. However, their work remained far from commercial utility as the maximum turnover numbers obtained in the ethenolysis of pure methyl oleate were about 3,000.[4,5] Therefore, we started a program to identify the most promising ethenolysis catalysts, develop improved catalysts and optimize ethenolysis process conditions. This program was divided into the following tasks:

- *Task 2a. Preliminary catalyst and feedstream screens*
- *Task 2b. Studies of catalyst activity loss*
- *Task 2c. Catalyst development and modification*
- *Task 2d. Process optimization and scale-up*
- *Task 2e. Synthesize metathesis products and product derivatives.*

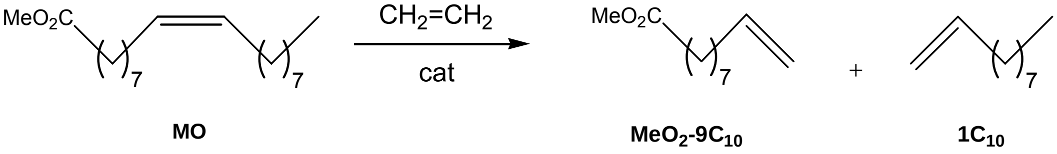
Our research and development efforts resulted in the identification of the most promising existing metathesis catalysts and of reactivity trends amongst the different categories of metathesis catalysts. Additionally, better understanding was gained regarding different factors that limit the efficiency of the ethenolysis reaction, including the nature of the substrate as well as the role and mode of catalyst decomposition. The catalyst modification work led to the development of improved systems, while the process optimization and scale-up part of the program provided useful data for building engineering models and estimating process economics, as well as substantial amounts of 9-decenoic acid needed for application development activities. Finally, additional metathesis reactions were explored to further derivatize 9-decenoic acid.

Results

Task 2a. Preliminary catalyst and feedstream screens

Existing metathesis catalysts were first screened in the ethenolysis of model substrate methyl oleate (received from Nu-Chek-Prep) under mild temperatures (30-40 °C), relatively low ethylene pressure (120-180 psi) and different catalyst concentrations (detailed data is given in Appendices F and G).

The ethenolysis of methyl oleate consists of subjecting neat methyl oleate to an olefin metathesis catalyst under a pressure of ethylene to induce the cleavage of the substrate's double bond and therefore produce two terminal olefins: methyl-9-decenoate (MeO_2-$9C_{10}$) and 1-decene ($1C_{10}$) (see Scheme 1).



Scheme 1: Ethenolysis of methyl oleate.

Metathesis catalysts representative of different classes such as 1st generation Grubbs (i.e., C823 and C801) and Hoveyda-Grubbs (i.e., C601) catalysts, 2nd generation Grubbs (i.e., C848 and C933) and Hoveyda-Grubbs (i.e., C627 and C712) catalysts, as well as 1st and 2nd generation bis-pyridine catalysts (i.e., C679 and C727, respectively) were included in the initial screens. Drawings of these catalysts are shown in Appendix E.

1st generation Grubbs catalyst C823 showed fair activity in the ethenolysis of methyl oleate giving moderate to good yields when used at loadings of 100 ppm and above (see Figure 1). A maximum turnover number (TON) of 25,000 is obtained with 10 ppm of C823 (see Figure 2). C823 is very selective towards ethenolysis: the main side-products generated in the process are products of self-metathesis of methyl oleate (e.g., the trans isomer of methyl oleate or methyl elaidate; trans-1,18-dimethyl-9-octadecenedioate; and trans-9-octadecene). These side-products are formed in small amounts especially at low catalysts loadings. For example, the ethenolysis of methyl oleate promoted by 100 ppm of C823 (40 °C; 150 psi ethylene; 56 % yield after 2 h) produces about 1.6 % of 1,18-dimethyl-9-

octadecenedioate and 1.6 % of 9-octadecene, while the reaction catalyzed by 35 ppm of C823 (40 °C; 150 psi ethylene; 45 % yield after 4 h) produces only 0.7 % of each 1,18-dimethyl-9-octadecenedioate and 9-octadecene (see Appendices G1 and G2).

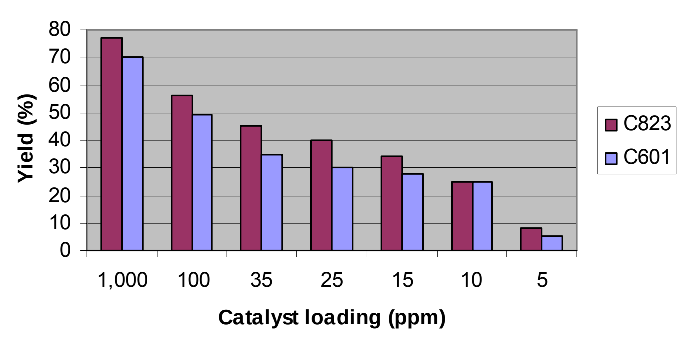


Figure 1: Ethenolysis yields versus catalyst loadings for catalysts C823 and C601

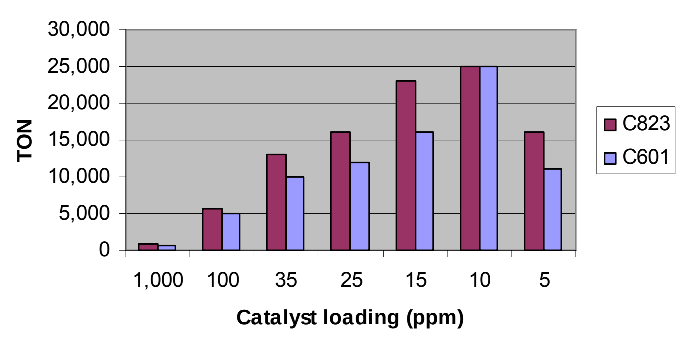


Figure 2: Ethenolysis TONs versus catalyst loadings for catalysts C823 and C601

1st generation Hoveyda-Grubbs catalyst C601 proved faster than C823. Indeed, C601 tends to reach maximum conversion within 30 minutes, while it usually takes 2 hours for C823 to reach its conversion plateau (see Appendices G1-G4 for ethenolysis kinetic data). However, C601 generally gives slightly lower yields than C823 (except at 10 ppm, where C601 and C823 give the same yield of 25 % and therefore the same maximum TON of 25,000; see Figures 1 and 2). These results suggest that C601 initiates faster than C823 but that it may also decompose faster.

2nd generation Grubbs catalyst C848 and Hoveyda-Grubbs catalyst C627, which are very active in the self-metathesis of methyl oleate, were found to give lower yields than their 1st generation equivalents in the ethenolysis reaction. The ethenolysis of methyl oleate catalyzed by 100 ppm of C848 reaches a plateau after 2 h to give only 28 % yield affording more self-metathesis products than ethenolysis products (see Appendix G5). The ethenolysis catalyzed by C627 reaches a plateau in less than 15 min, but gives similar results: 20 % yield of ethenolysis products and a majority of self-metathesis products (see Appendix G6). Based on these results, we believe that C848 and C627 are less selective towards ethenolysis than their 1st generation equivalents C823 and C601. More specifically, it seems that 1st generation catalysts give ethenolysis reaction mixtures that correspond to kinetic product distributions with a selectivity towards ethenolysis products, while 2nd generation catalysts are not kinetically selective but tend to yield reaction mixtures that correspond to thermodynamic product distributions.

2nd generation catalysts C933 and C712, which contain a more sterically hindered N-heterocyclic carbene (NHC) ligand, seem more selective than C848 and C627 and give higher ethenolysis yields. Indeed, ethenolysis using 100 ppm of C933 and C712 reach plateaus of 36 % and 39 % yield, respectively, within 30 minutes (see Appendices G7 and G8). In fact, C933 gives 25 % yield of ethenolysis products at 10 ppm loading, which corresponds to a maximum TON of 25,000, equal to that obtained with C823 and C601 (see Table F3 in Appendix F).

Finally, bis-pyridine catalysts C679 and C727 showed relatively poor activity in the ethenolysis of methyl oleate (see Table F2, entries 28-29 and Table F3, entry 16), which is presumed to result from poor solubility in the oil. Bis-pyridine catalysts were therefore not further investigated.

Upon completing these initial catalyst screens, we set out to screen different qualities and types of oils. We first examined the effect of further purifying the pure methyl oleate obtained from Nu-Chek-Prep on the ethenolysis yields. The methyl oleate was filtered through and stored over activated alumina. Both research grade methyl oleate as received from Nu-Chek-Prep and further purified material were subjected to ethenolysis conditions using 5, 10, 15, 25 and 35 ppm of C823. For the highest catalyst loading tested (35 and 25 ppm) the yields obtained with both materials were identical (45 and 40 %, respectively) (see Table F1, entries 23-26). However, for the lower catalyst loadings, the yields obtained with the purified material were higher than those with non-purified material (see Table F1, entries 21,22 and 27-30). Furthermore, the results show that the lower the catalyst loading the larger the effect of purification. These data suggest that a poison (i.e., an impurity responsible for the death of the catalyst) is removed, at least partially, via the treatment with alumina. As lower catalyst loadings are used, the amounts of poison relative to the amounts of catalyst are larger and the effect of purification on the yields is greater.

The next oil to be studied was technical grade methyl oleate (70 %), which was subjected to ethenolysis using C823 as the metathesis catalyst under an ethylene pressure of 180 psi and at 40 °C (see Appendix H for more details on procedure). It was determined that technical grade methyl oleate generally requires higher catalyst loading than pure methyl oleate to achieve good conversions. Indeed, the ethenolysis of non-purified Cognis methyl oleate using a catalyst loading of 1,000 ppm (0.1 mol %) gave only 56 % yield. Although we found that the treatment of the oil with activated alumina improved the catalyst efficiency, purified technical grade methyl oleate still required more catalyst than pure grade methyl oleate. For example, the ethenolysis of purified Cognis methyl oleate gave only 20 % yield with 100 ppm of C823 and 52 % yield with 500 ppm (see Table H1, entries 5-6) compared to 69 % for pure grade methyl oleate with 100 ppm C823 under the same conditions (see Table F1, entry 10). The highest turnover numbers were obtained for the technical grade methyl oleate from Nu-Chek-Prep: TON of 3,600 with 100 ppm C823 (36 % yield) and TON of 1,340 with 500 ppm (67 % yield) (Table H1, entries 7 and 8). One of the most logical explanations for the lower yields obtained with technical grade material versus pure grade material is that catalyst poisons are present in the lower grade oils.

Other fatty acid methyl esters (i.e., fatty acid methyl esters of soybean and canola oil) were tested in ethenolysis catalyzed by C823. Similarly to what was observed for technical grade methyl oleate, these substrates required the use of relatively high catalyst loadings (e.g., 350 ppm of C823 per substrate double bond) to give yields around 50 % at best (see Appendix I).

Additionally, triacylglycerides such as soybean, canola, peanut, palm, linseed, and sunflower oils were screened in ethenolyses using different catalysts. Trends similar to those observed with the ethenolysis of pure methyl oleate were found: C823 is slightly more efficient than C601 and the yields obtained with C712 are comparable to those obtained with C823 and are higher than those given by C627. Again, the ethenolysis of triacylglycerides necessitates relatively high catalyst loadings: for example, the ethenolysis of soybean oil catalyzed by 110 ppm of C823 per double bond of substrate gave an estimated yield of 24 %, while 440 ppm resulted in 39 % yield (see Appendix J; Table J1, entries 1 and 3). Moreover, we determined that soybean oil treated with activated alumina gave the best results (i.e. 50 % yield with 220 ppm of C823; see Table J1, entry 16). Canola oil was found to behave comparably to soybean oil, while peanut, palm, linseed and sunflower oil gave poorer results than soybean and canola oil.

Finally, the use of conjugated methyl linoleate (CML) as an ethenolysis substrate was investigated. Ethenolysis of conjugated methyl linoleate is Confidential Information.

Task 2b. Studies of catalyst activity loss

As described above, all ethenolysis reactions studied under task 2a reach a maximum conversion level in about 2 hours or less depending on the catalyst used. Additionally, the maximum conversion levels decrease as the catalyst loadings are lowered. Although, this type of behavior indicates that catalyst decomposition is taking place while the ethenolysis reaction is proceeding, there are other potential factors responsible for limiting the overall reaction efficiency including: a) the intrinsic polar nature of the substrate (the presence of ester functionalities in the substrate, which could coordinate to the ruthenium center and reduce the catalyst overall activity), b) the inhibition of the catalyst via binding of ethylene and ethenolysis products (terminal olefins) by the ruthenium centers, and c) non-productive side metathesis processes that tie up some of the catalyst species in the form of stable non-ethenolysis intermediates. We decided to investigate the involvement of these different factors in the ethenolysis process.

First, the ethenolyses of non-polar E-9-octadecene and Z-9-octadecene catalyzed by C823 (100 ppm; 40 °C; 150 psi ethylene) were studied. The ethenolysis product of these reactions (1-decene) was obtained in 39 % in the case of E-9-octadecene and 55 % yield in the case of Z-9-octadecene (56 % yield was obtained for the ethenolysis of methyl oleate under the same conditions), suggesting that the configuration of the carbon-carbon double bond has a strong influence on the ethenolysis efficiency while the presence of the polar ester functionalities does not seem to slow the reaction down nor lower the final yields (see Appendix L).

The catalyst inhibition by ethenolysis products had recently been proposed as a major factor in the catalyst activity loss by Maughon and coworkers.[6] However, our results related to the ethenolysis of 9-octadecene/1-decene mixtures (see Appendix M) reveal that higher ethenolysis conversions are reached when the initial substrate mixture contains more ethenolysis products (i.e., 1-decene). This suggests that catalyst inhibition seems to be a smaller factor than catalyst decomposition. Additionally, a set of experiments was conducted on pure methyl oleate, where this substrate was subjected to ethenolysis conditions with C823 (200 ppm; 40 °C; 150 psi ethylene) for a period of time before refilling the reactor with an additional equal volume of methyl oleate and re-subjecting the new mixture (which corresponds to an effective catalyst loading of 100 ppm) to ethenolysis (see Appendix N). For example, the experiment where the reactor was refilled with methyl oleate after 2 hours of initial ethenolysis shows that the final conversion level (44 % yield) is much lower than that reached when 100 ppm of catalyst was added at ounce at the beginning of the process (56 % yield). Similarly, even lower final conversion levels are obtained as the refill is conducted at 3 and 4 hours. After 4 hours, there seems to be very little catalytic activity left. These results are consistent with the presumption that the activity loss is mainly related to catalyst decomposition occurring during the ethenolysis process and not so much to catalyst inhibition (under the used conditions and within the observed time frame).

Therefore, we set out to explore the catalyst decomposition modes under ethenolysis conditions. In the absence of decomposition induced by impurities in the substrate and solvent, the most likely potential decomposition pathways include (a) an attack of a nucleophile (e.g., phosphine in 1st and 2nd generation Grubbs catalysts) on the ruthenium methylidene and ruthenium alkylidene species;[7, 8] (b) unimolecular decomposition of the ruthenacyclobutane intermediate via β-hydride elimination followed by reductive elimination to produce propene;[9] (c) C-H activation of the phosphine or N-heterocyclic carbene;[7, 10] and (d) bimolecular decomposition of the ruthenium methylidene or ruthenium alkylidene species to produce an internal olefin and a diruthenium decomposition product.[7, 11]

It was established that 1st generation Grubbs catalysts (e.g., C823) are quickly converted into the ruthenium-methylidene species C747 in presence of ethylene even at low pressures, so we focused our decomposition studies of 1st generation Grubbs catalysts on C747. Decomposition of C747 was studied in the presence of ^{13}C-labeled ethylene in order to facilitate NMR identification of the decomposition and potential inhibition products (see Appendix O for detailed experimental procedures). No ruthenium-ethylene π-complex was observed by ^{13}C and ^{1}H NMR. $^{13}CH_3PCy_3Cl$ was identified as the sole labeled species resulting from decomposition, which led us to conclude that nucleophilic attack of the free phosphine onto the ruthenium-methylidene is the main pathway of 1st generation Grubbs catalyst decomposition in ethenolysis. The same methylphosphonium salt had previously been observed by Grubbs et al. in 1st generation and 2nd generation Grubbs systems.[7, 8]

The phosphine-free 1st generation Hoveyda-Grubbs catalyst C601 was then studied in its reaction with ^{13}C-labeled ethylene. The only labeled species present during and after catalyst decomposition were 2-isopropoxystyrene (arising from the reaction of C601 with ethylene during normal metathesis cycle) and ethylene itself. This suggested the possibility that ethylene, while being the starting material in the reaction, may also be the product of decomposition of the 14-electron ruthenium-methylidene via the bimolecular pathway.

An experiment was then designed to measure the catalyst decomposition rate under conditions closely approximating those used during actual ethenolysis (40 °C, 150 psi ethylene; see Appendix O). Decomposition of C601 was then studied at different catalyst concentrations to test the bimolecular decomposition hypothesis. Figure 3 illustrates the combined decay of all ruthenium-alkylidene species at different concentrations and shows no dependence of the catalyst decomposition rate on the catalyst concentration. This discounts the possibility of decomposition via the bimolecular mechanism and suggests that it is instead a unimolecular process, at least under ethenolysis reaction conditions and within the range of concentrations studied. An alternative explanation for the absence of a ^{13}C-labeled decomposition product in the reaction of C601 and labeled ethylene may involve a paramagnetic ruthenium complex, unobservable by NMR spectroscopy.

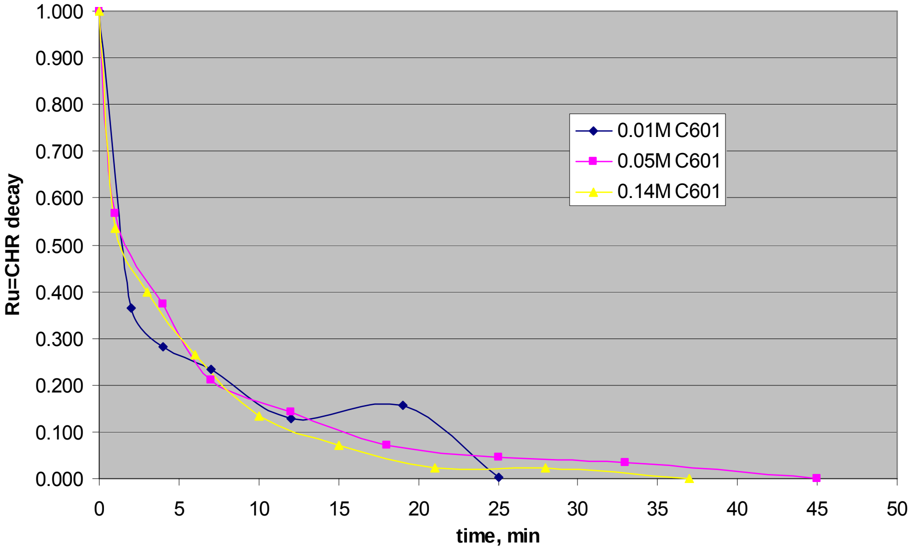


Figure 3: Normalized C601 decomposition rate at 40 ^{o}C and 150 psi of ethylene

We have also compared the rate of C601 decomposition under different ethylene pressures (which result in different concentrations of ethylene in solution and therefore different rates of ruthenium-methylidene formation) and, separately, in presence of a terminal olefin (1-hexene, 14 molar equivalents) in the amount corresponding to ethylene/C601 ratio under normal ethenolysis conditions. The results of this study clearly indicate that ruthenium-methylidene species is the main reason for fast catalyst decomposition in ethenolysis (see Figure 4). Faster ruthenium-methylidene formation results in faster decomposition (compare 1 atm vs. 150 psi ethylene). Using a terminal olefin in place of ethylene results in a marked slowdown of catalyst decomposition (compare 150 psi ethylene vs. 14 equiv 1-hexene), presumably due to the fact that half of the catalytic species undergoing metathesis is now the more stable ruthenium-alkylidene rather than ruthenium-methylidene.

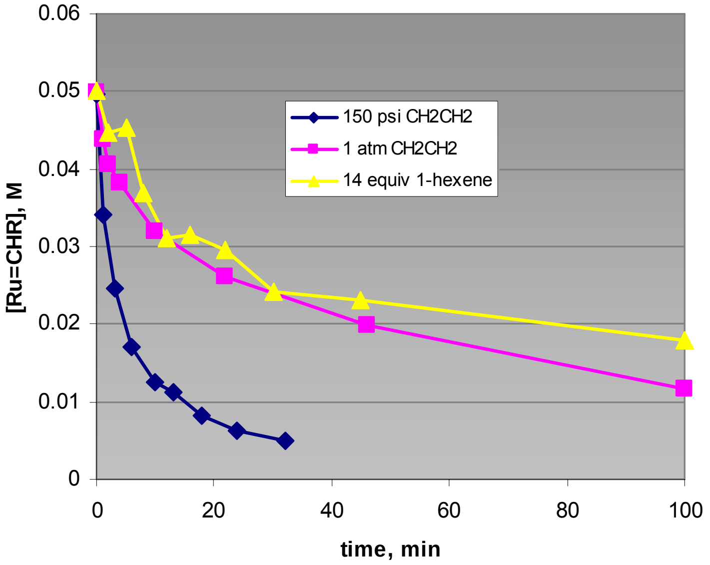


Figure 4: Decomposition of C601 (0.05 M) in presence of ethylene and 1-hexene

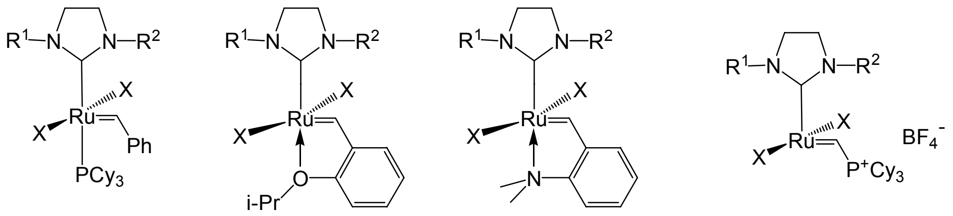
Decomposition of 2nd generation Grubbs-Hoveyda catalysts C627 and C712 has also been studied using both ^{13}C-labeled ethylene and normal ethenolysis conditions. Once again, the only ^{13}C-labeled species observed in the reactions were 2-isopropoxystyrene and ethylene. We have also observed that the NMR resonances corresponding to the NHC ligands in both C627 and C712 disappear concurrently with the decomposition of ruthenium-alkylidene species (which was slower in case of C712). The products of the NHC ligand degradation could not be identified by NMR spectroscopy. During the study of the rate of C712 decomposition under 150 psi ethylene we have observed several new unidentified resonances in the ^{1}H NMR spectrum, that seem to indicate formation of an unknown ruthenium-alkylidene species (δ_H 25.6 ppm) and several ruthenium-hydride species (δ_H 0 to -8 ppm). These observations are consistent with decomposition via C-H activation, which we believe is the main contributor to the decomposition of 2nd generation Grubbs-Hoveyda catalysts in ethenolysis.

These findings on catalyst decomposition have fundamentally improved our understanding of the factors that are limiting the catalyst efficiency in the ethenolysis reaction and will serve as a guiding light for the development of improved seed oil ethenolysis processes. In particular, we submit that it would be especially interesting to develop more robust and thus longer-lived olefin metathesis catalysts.

Task 2c. Catalyst development and modification

A study of the effect of additives on catalyst activity was conducted with different classes of additives such as bases (e.g., pyridine), Brönsted acids (e.g., acetic acid and hydrochloric acid), Lewis acids (e.g., copper(I) chloride, tris-isopropoxide aluminum(III) and methyl aluminoxane or MAO) and anti-oxidants (e.g., bis-t-butylhydroxytoluene or BHT). The results showed that the addition of pyridine or a Lewis acid is detrimental, while the addition of Brönsted acids or BHT leads to incremental, but measurable improvements in turnover number (see Appendix R). As such, the sheer use of additives does not seem to provide a sufficient solution to make seed oil ethenolysis an economical process. Therefore, we decided to pursue the development of improved ethenolysis catalysts.

The initial phase of the catalyst development program involved the synthesis and testing of complexes with varying steric environments, based on the fact that 2nd generation systems are highly active metathesis catalysts but not very selective towards ethenolysis and on the observation that 2nd generation catalyst that contain a larger NHC ligand tend to be more selective towards ethenolysis (i.e., C933 and C712 are more selective than C848 and C627; see section on Task 2a). New complexes of Grubbs, Hoveyda-Grubbs, Materia and Piers type with various substituents on the nitrogen atoms of the NHC ligand and various anionic ligands were synthesized and tested (see Scheme 2 and Table 2).

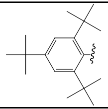
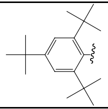
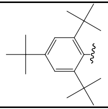
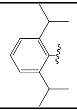
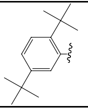
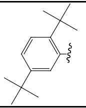
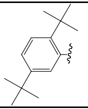
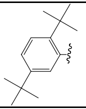
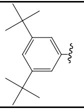
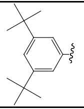
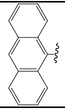
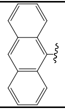
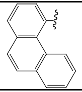
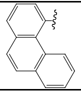
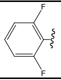
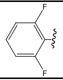
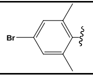
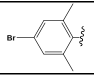
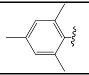
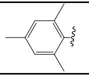
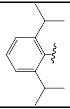
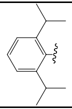
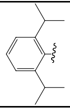
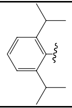
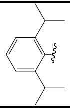
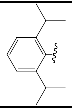
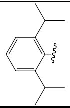
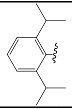
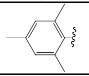
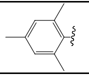


Grubbs **Hoveyda** **Materia** **Piers**

Scheme 2: Different types of catalysts tested during initial phase of catalyst development

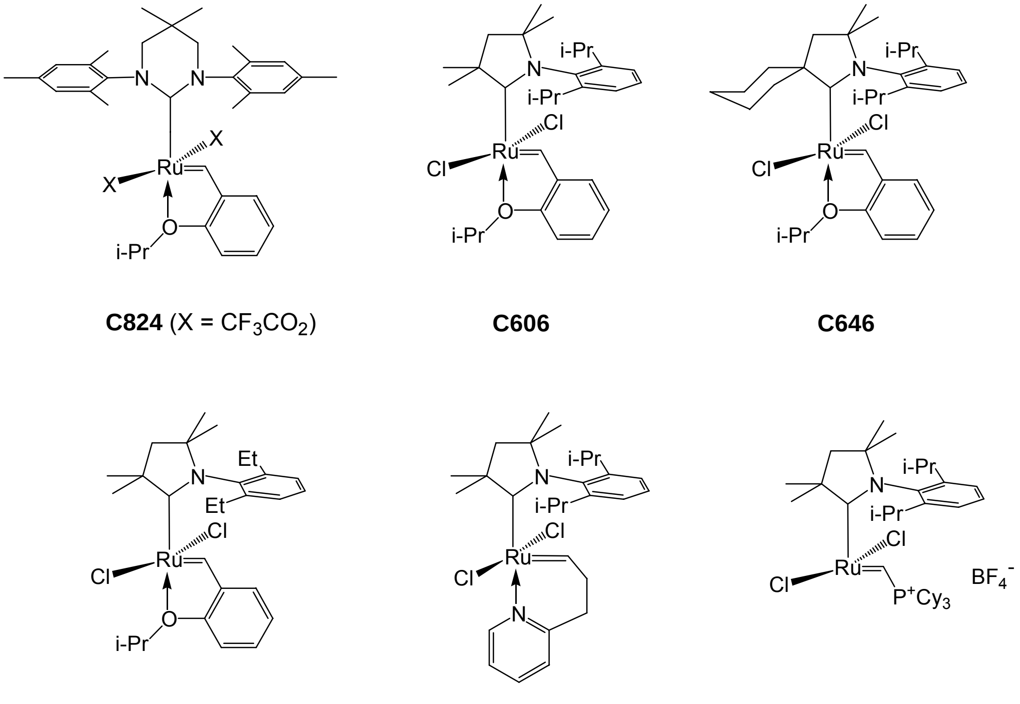
The results of this study revealed that it is important that the bulky substitutents on the aryl groups of the NHC ligands be attached to the ortho positions in order to impart greater selectivity to the catalysts. Additionally, it was shown that complexes that contain NHC ligands substituted with flat aryl groups such as those derived from anthracene and phenanthroline (e.g., catalysts C965-A and C965-P) are less selective than C848, presumably due to the fact that these flat aryl groups exert less steric pressure on the catalyst active site than 2,4,6-trimethylphenyl (or mesityl) rings.

Table 2: Substitutions on catalysts tested during initial phase of catalyst development

Cat #	R^1	R^2	X	Cat. type	Comments
NA			NA	NA	Ligand synthesis was not successful
NA			NA	NA	Ligand synthesis was not successful
C989			Cl	Grubbs	Less selective than C848
C767			Cl	Hoveyda-Grubbs	More selective than C627
C767-M			Cl	Hoveyda-Grubbs	Less selective than C627
C965-A			Cl	Grubbs	Much less selective than C848; requires high temp.
C965-P			Cl	Grubbs	Less selective than C848; requires high temp.
C837			Cl	Grubbs	Much less selective than C848
C880			Cl	Grubbs	Much less selective than C848
C978			Cl	Grubbs	Much less selective than C848
C782			F_3CCO_2	Hoveyda-Grubbs	More selective than C627
C866			F_3CCO_2	Hoveyda-Grubbs	**Very selective; more selective than C712**
C697			Cl	Materia	More selective than C627, but much slower
C785			Br	Materia	More selective than C627, but much slower
C879			I	Materia	More selective than C785, but also very slow
C859			Cl	Piers	More selective than C848, but much slower

Moreover, we found that the substitution of bulky anionic groups such as trifluoroacetate (F_3CCO_2 group) and larger halides (i.e., bromide and iodide) for the chlorides also improved the selectivity of the catalysts towards ethenolysis (see for examples, results with C782). In fact, the combination of bulky NHC ligand and bulky anionic ligands as in complex C866 gives a very selective catalyst (selectivity around 90 %; see Appendix S, Table S2, entries 15-17). Finally, the complexes of Materia and Piers types were found to be more selective but also much slower than C848 and C627 (see Table 2 above and Table S2 in Appendix S).

A second phase of the catalyst development program involved the synthesis and testing of 2nd generation complexes that contain different N-heterocyclic carbenes such as 6-membered ring NHC ligands and Bertrand[12] NHC ligands. Among others, complexes C824, C606, C646, C578, C577 and C838 were studied (see Scheme 3 and Table S2 in Appendix S).



C824 (X = CF_3CO_2) **C606** **C646**

C578 **C577** **C838**

Scheme 3: Different catalysts tested during second phase of catalyst development

Complex C824, which contains a 6-membered ring ligand, was shown to be highly selective towards ethenolysis but gave relatively poor yields (86 % selectivity, 30 % yield at 100 ppm catalyst loading; see Table S2, entry 29). We believe that this complex is more selective because the 6-

membered ring ligand exerts more steric pressure on the system but that it is less stable and decomposes relatively rapidly.

Of all the catalysts that contain Bertrand NHC ligands (e.g., C606, C646, C578, C577 and C838), C578 is the most noteworthy as it is highly selective and gives very high TON. Indeed, the use of 10 ppm of C578 affords a 35 % yield in less than 30 minutes in the ethenolysis of methyl oleate corresponding to a turnover number of 35,000 and a turnover frequency greater than 1,000 min^{-1}, and a 42 % yield after 1 hour or a 42,000 TON.

Task 2d. Process optimization and scale-up

It was established from the work conducted under Task 2a, that C823 is one of the most promising catalysts for the ethenolysis process. Indeed, C823 gives some of the highest TON and is amongst the lesser expensive olefin metathesis catalysts. Therefore, we decided to focus our process optimization efforts on finding the optimal conditions (i.e., ethylene pressure and reaction temperature) for ethenolyses catalyzed by C823.

The dependence of the ethenolysis process on ethylene pressure was initially studied over a wide range of pressure (30-800 psi) and it was determined that C823 performs better at intermediate pressures (i.e., between about 70 and about 200 psi) rather than at low (i.e., 30 psi) or high (i.e., 800 psi) pressures (see Appendix T). The pressure dependence was subsequently studied over a narrower range (60-360 psi) and the results revealed that pressures between 120 and 180 psi seem optimal (see Figure 4 and Table F1, entries 1-4).

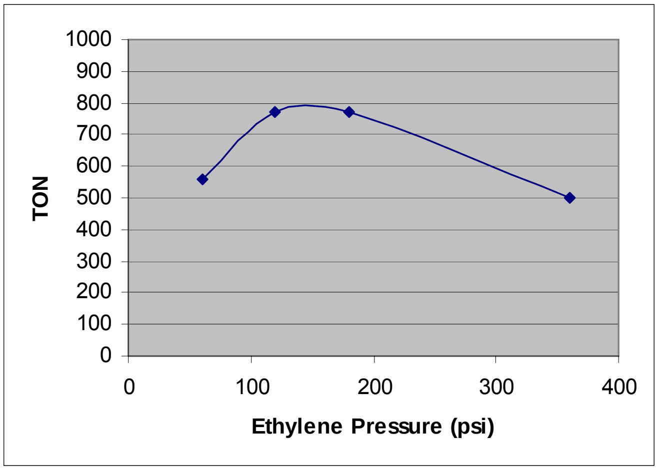


Figure 4: Pressure dependence of ethenolysis of methyl oleate using C823 (0.1 mol %) at 30 °C

We then showed that the ethenolysis efficiencies also depend on the reaction temperature and that optimal temperatures range from 30 to 40 °C (see Figure 5 and Table F1, entries 3 and 5-8).

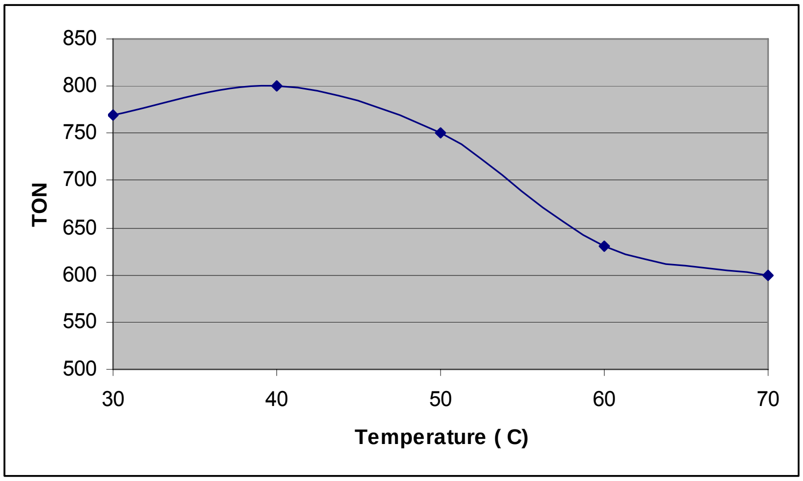


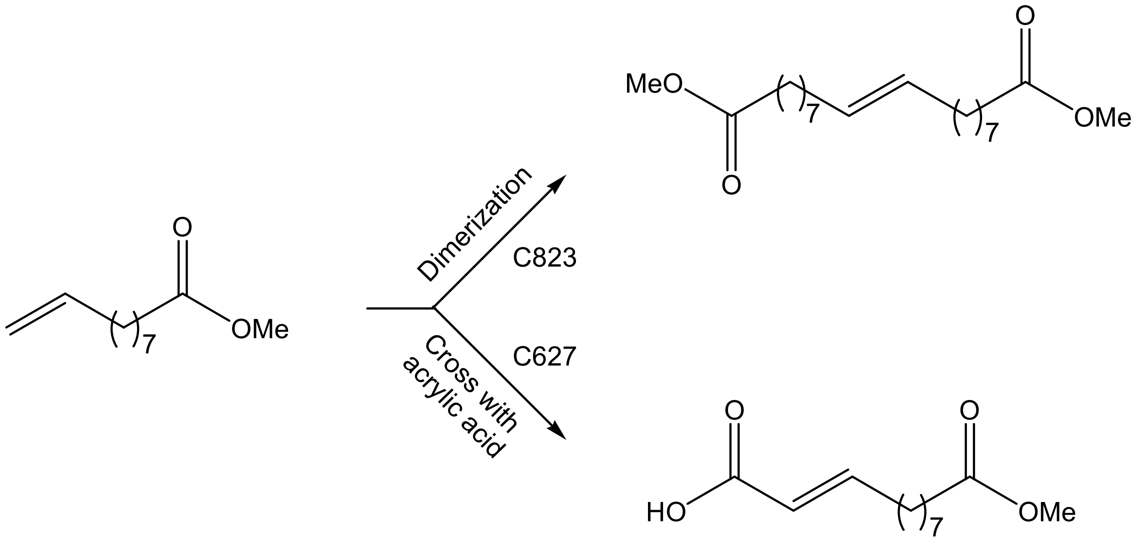
Figure 5: Temperature dependence of ethenolysis of methyl oleate using C823 (0.1 mol %) at 180 psi

Interestingly, we also found that, contrary to 1st generation systems, 2nd generation catalysts perform better at higher pressures (see Appendix U), which is consistent with the idea that 2nd generation catalysts tend to give reaction mixtures that correspond to thermodynamic product distribution. Indeed, the thermodynamic equilibrium of the ethenolysis reaction lies more towards ethenolysis products at higher ethylene pressures than at lower pressures.

Subsequent efforts under this task involved scaling up the ethenolysis of soybean oil in order to demonstrate industrial feasibility, generate data for building engineering models and estimating process economics, and provide substantial amounts of 9-decenoic acid for application development activities. Therefore, ethenolyses of soybean oil were successively run at 1 L, 10 gal and 30 gal scales in 2 L and 50 gal reactors. The runs in the 50 gal reactor gave the best results with estimated methyl 9-decenoate yields of 34 and 37 % at the 10 gal and 30 gal scales, respectively. Finally, the soybean oil ethenolysis was scaled-up to 100 gal and the ethenolyzed soybean oil was shipped to Cargill. The ethenolyzed soybean oil was worked up to afford about 100 pounds of 9-decenoic acid.

Task 2e. Synthesize metathesis products and product derivatives

Methyl 9-decenoate obtained from the ethenolysis process was subsequently derivatized by further metathesis to make precursors of the linear C18 and C11 diacids. In the first case, methyl 9-decenoate was successfully homo-dimerized by olefin metathesis using C823 to give the linear C18 diester. In the second case, methyl 9-decenoate was cross-metathesized with acrylic acid using C627 to give the linear C11 mixed acid-ester in high yield (see Scheme 2). While these reactions demonstrate the feasibility of further derivatization of methyl 9-decenoate via metathesis, the processes need to be optimized.



Scheme 2: Metathesis products from methyl 9-decenoate

Technical Summary of Task 4

Introduction

A process model was built in Aspen Custom Modeler (ACM) using Cargill's proprietary, in-house model library and, potentially, with additional algorithms developed specifically for this process. These models have initially performed simple energy and mass balance growing with the project to encompass detailed reactor and separation performance. Model performance and results assisted in directing lab-scale and pilot-scale research as well as commercial-scale design. Relevant chemical information including physical properties are stored in the model. More detailed process models will include heat, water, solvent, co-product, and waste stream integration in the process.

The process models will be linked to Cargill's proprietary costing algorithms enabling the rapid calculation of process-change impacts on project economics during the process synthesis and process development stages. Economic detail level will be commensurate with process understanding.

A more detailed description of the proposed deliverables follows.

a. Develop preliminary metathesis reactor model. Deliver a report detailing the reaction kinetics and produce a mathematical representation in a process simulation software package.
b. Build physical properties database, identify gaps in existing knowledge, and propose means to acquire additional data. This subtask may include experimental determination of physical properties as needed.
c. Propose and close mass balances multiple process designs. Deliver a report containing process flowsheets and a description of the various unit operations contained in the process. Produce a mathematical representation in a process simulation software package. Separation schemes proposed in the process design may include lab-scale testing.
d. Perform high-level economic analysis on multiple process designs and deliver a report.
e. Develop biocatalytic process model. Deliver a report detailing the reaction kinetics and produce a mathematical representation in a process simulation software package.
f. Apply product specification based on end-use application into product purification scheme. List product specifications and report impact on process economics.
g. Incorporate process in context of a oilseed processing site. Deliver a process model.
h. Perform overall economic evaluation. Report results.

Tasks 4e, 4f, 4g, and 4h were not pursued due to funding reduction by the DOE and refocusing of project priorities on metathesis chemistry development. Technical summaries of Task 4 subtasks follow.

4a) Develop preliminary metathesis reactor model. Deliver a report detailing the reaction kinetics and produce a mathematical representation in a process simulation software package.

This subtask, 4a, outlined as the preliminary reactor modeling activity naturally evolved into means to interpret experimental data and delve into fundamental and mechanistic phenomena at the heart of applying successfully ethenolysis technology. The modeling effort collected experimental data, tested the proposed hypothesis generated by the team of experts via an applied model, aided in experimental design, and predicted outcomes. Areas of investigation included describing the reaction kinetics, developing a probabilistic reaction product mixture model to evaluate the performance of the impure commodity feedstocks, test phase equilibria questions, and test novel reactor designs to overcome some of the limitations uncovered in simple batch reactor experimentation.

Discussions were started with Materia on detailed reaction mechanisms for ethenolysis of methyl oleate. Possible catalyst intermediates, transition states, and decomposition pathways were identified. A literature search was performed to understand past work on the subject. The reactor model developed includes a representation that allows for estimating various metathetical co product concentrations resulting from feedstock impurities and incomplete reaction conversion.

In order to evaluate effectively various oilseed biorefinery concepts, a general metathesis reactor model that can predict statistical equilibrium for various reactions was developed. Metathesis reactions with vegetable oil or its derivatives as the feedstock are very complicated, since it can produce many products. For example, the baseline metathesis reaction of soybean oil fatty acids can result in more than 100 different components. Since separation schemes will vary depending on the co-products produced, it is essential to have a general metathesis model for preliminary process design. This model was developed assuming statistical equilibrium, i.e. assuming that every double bond has an equal chance of reacting with another double bond. This generalized model has been shown to be effective at predicting equilibrium for various metathesis reactions, and will continue to be used as we further explore the biorefinery concept.

The model was integrated into the Aspen Custom Modeler (ACM) software, and can link to costing tools developed in Microsoft Excel in order to assess economic viability. A model for the production of caproleic acid product by the ethenolysis of a commodity oil derived feedstock was developed using the Aspen Custom Modeler (ACM) platform. A preliminary cost estimate (+100%/-50%) was completed for the production at a large scale. This base case cost model does not yet include co-product descriptions. The analysis identified several areas that require additional work:

- Additional experimental data to determine catalyst loadings necessary for the ethenolysis of different grade feedstocks.
- Model the side products produced by the ethenolysis reaction and downstream separation.
- Study system effects dependent on reaction yield.

Ethenolysis of renewable oils and oil derivatives involves the transfer of gaseous ethylene to the liquid-phase reaction. A well mixing of ethylene gas into liquid oil is essential for the economic metathetical conversion. We have tested two specially designed reactor concepts intended to drive ethenolysis conversion of soybean oil or methyl oleate with ethylene gas in the presence of Grubb's catalysts.

Reactor Concept 1 was tested on a lab-scale device with the reactor equipment vendor. The scope of the activity was to perform a quick scan applying the novel reactor design to understand the impact of design on overall ethenolysis economics. Multiple attempts were made to demonstrate the reactor effectiveness but each experiment suffered from premature catalyst deactivation. The experimental work was halted due to the experimental complexity of this particular proposal.

Reactor Concept 2 was tested via computer simulation partnering with an external engineering firm. The external firm tested the processing concept applying physical property data and estimates of reaction velocity provided by the Cargill team to test a reactive separation design concept. After several iterations between the process, chemistry, and engineering teams, the consensus reached was that the proposed design had critical flaws due to the physical properties of the system and the separation requirements. The study was terminated with a relatively small investment but gaining critical insight.

4b) Build physical properties database, identify gaps in existing knowledge, and propose means to acquire additional data. This subtask may include experimental determination of physical properties as needed.

We explored the feasibility of contracting experiments and/or molecular simulations in order to obtain VLE data needed to define the separation train for the metathesis system. Resources available to address the data generation in the time frame of the project had proposed budgets exceeding our existing project. The team concluded that this task could not be addressed adequately by the existing budget and was necessarily cancelled from this project.

Instead, a physical property database was built based on physical properties available in Aspen Plus, DECHEMA, and literature. Physical properties of many olefinic compounds, such as ethylene and 1,4-pentadiene, were widely available. Properties of compounds that were not available, such as caproleic acid methyl ester, were estimated with known properties of compounds with similar chain length and functionality. Empirical correlations of vapor pressure for different chain length olefins and esters were also developed to estimate VLE.

4c) Propose and close mass balances multiple process designs. Deliver a report containing process flowsheets and a description of the various unit operations contained in the process. Produce a mathematical representation in a process simulation software package. Separation schemes proposed in the process design may include lab-scale testing.

Two process concepts were modeled. One explored the ethenolysis of soybean and the other examined ethenolysis of methyl soyate, both in the production of 9-decenoic acid. Both models explored the impact on production costs as impacted by raw materials costs, catalyst use and yield. The first model was applied to supporting the pilot-scale production of 9-decenoic acid. The second process was used for the preliminary cost estimate (+100%/-50%) for the production at a large scale as described above.

Scope was added to the project in the testing of ethenolysis at the pilot scale. A processing plan was compiled for the metathesized SBO product mixture including the separation of 9-decenoic acid from other compounds. This involved coordinating the knowledge from various internal resources around the associated unit operations, as well as Materia's processing experience, and then locating a capable toller who could pilot the process. Necessary EHS and shipping requirements were addressed as well as transfer of appropriate analytical methods. The task will provide some direct supervision of the tolling process, specifically the less defined separation processes. This activity met the milestone for the production of 100lb of 9-decenoic acid.

4d) Perform high-level economic analysis on multiple process designs and deliver a report.

Several high-level economic analyses were done:

a) Preliminary cost estimate (+100/-50%) for the production of caproleic acid via ethenolysis of methyl soyate.

b) Evaluate economics of using different oils (canola, palm, soy, high oleic) to produce 9-decenoic acid

c) Evaluate economics of toll-scale production based on ethenolysis of soybean oil at current yields and catalyst loadings.

Toll Results

The concept explored is based on metathesizing an unsaturated oil (in this case soy) with ethylene to form a reaction product containing triglycerides of 9-DA. This reaction product was transesterified to form methyl esters, from which the 9-DA methyl ester was distilled and hydrolyzed to reform 9-DA.

A batch tolling process to produce at least 100 lb of 9-DA was investigated based upon previous smaller scale results describing the metathesis of soybean oil with ethylene and subsequent product separations. This included defining the major process steps and distillation cuts to be made, troubleshooting foaming in the hydrolysis, coordinating analytical support, and shipping/receiving of samples. Data necessary to fully describe the backend separations process was compiled to facilitate the creation of a process transfer package. Materia performed the larger scale metathesis reaction, with subsequent product separations including methanol transesterification, distillation, and hydrolysis performed by Pressure Chemical Company.

Larger scale production of 9-DA was accomplished as predicted by lab results. 9-DA was successfully produced at a 100-lb scale, although desired purity was found to be a factor for distillation yield of separated product.

An alternate processing pathway is to perform metathesis on the methyl esters of a vegetable oil, followed by a methanol transesterification to form the conceptually the same mixture of methyl esters that can then be distilled. One drawback of metathesis performed on a triglyceride is that during the transesterification step some product losses may occur on product, and it would, given equal metathesis yields and catalyst loadings, be better to have those losses be realized on material that hasn't already been metathesized.

Materia metathesized several batches of soybean oil under pressurized ethylene. Conversions measured were not as high as those obtained in the smaller scale lab work due to a loss of pressurization capability during a major run, but were still sufficient for the purposes of the pilot work. The resulting material was lightly stripped to stabilize the material and remove most hydrocarbons less than five carbons and shipped to Pressure Chemical. Pressure Chemical performed a batch methanol transesterification using a base metal as catalyst, similar to some processes found in biodiesel manufacturing. This process recovered the glycerin from the triglycerides and formed a second phase containing fatty acid methyl esters (FAME) and any residual hydrocarbons formed during metathesis. The FAME/hydrocarbon mixture was vacuum distilled to separate the components and recover 9-DA methyl ester at high purity. This process was successful. The 9-DA methyl ester recovered was then hydrolyzed using base-catalyzed hydrolysis. The residual methanol was stripped and recovered, leaving a pure cut of 9-DA.

Process conditions and product yields are well documented and available upon request from Cargill. The tasks successfully demonstrated 9-decenoic acid production at the 100-lb scale.

Conclusion

Upon completion of the five subtasks in Task 2 and four of the subtasks in Task 4, we have collected useful and important data related to the ethenolysis of seed oil-derived materials.

Under task 2a, commercially available and other Materia ruthenium-based olefin metathesis catalysts were screened in the ethenolysis of different oils to establish that the 1st generation Grubbs catalyst (C823) is one of the most economical systems, because it catalyzes the reaction in high turnover numbers (i.e., 25,000) and is amongst the least expensive ruthenium metathesis catalysts to produce. Additionally, different triacylglycerides (e.g., soybean, canola, peanut, and sunflower oils) and fatty acid methyl esters (e.g., different sources of technical grade methyl oleate, methyl soyate, and methyl canola) were screened and it was determined that the purity and the nature of the oils have a large influence on the catalyst efficiencies. In particular, the ethenolysis of technical grade triacylglycerides and fatty acid methyl ester were found to require much higher catalyst loadings than that of pure methyl oleate. Moreover, conjugated methyl linoleate was shown to be a very poor substrate for the ethenolysis catalyzed by current olefin metathesis systems.

Under task 2b, different potential factors that could limit catalyst activity were explored. It was determined that cis-olefins are better substrates than trans-olefins and that the presence of the ester functionalities in seed oils does not seem to slow down or limit the ethenolysis reaction. It was also established that catalyst inhibition by the ethenolysis products does not seem to be a major limiting factor but that substantial catalyst decomposition occurs as the ethenolyses proceed in all the studied cases (1st generation Grubbs, 1st generation Hoveyda-Grubbs and 2nd generation Hoveyda-Grubbs catalysts). The 1st generation Grubbs was shown to decompose via a pathway that involves the attack of a liberated phosphine ligand onto a ruthenium-methylidene species (an ethenolysis intermediate), while the Hoveyda-Grubbs catalysts were found to decompose by a unimolecular process which seem to involve C-H activation of the NHC ligands in the case of the second generation systems. The results of this task may be the basis for further development work, which should consist in the design and synthesis of more stable catalysts that do not partake in facile ligand C-H activation.

Improved ethenolysis catalysts were successfully developed under task 2c, which include more sterically hindered 2nd generation systems that proved more selective than traditional 2nd generation complexes as well as selective/robust systems based on Bertrand NHC ligands that give turnover numbers as high as 42,000. So far, only research quantities of these complexes have been produced and tested, which calls for further development of these catalysts.

Task 2d involved process optimization and scale up of the ethenolysis catalyzed by C823, which provided data such as optimal process parameters, as well as reaction kinetics and efficiencies useful to the development of engineering models and estimation of process economics (see Task 4). Additionally, 100 lbs of 9-decenoic acid was produced from soybean oil and directed towards application development activities.

Finally, the feasibility of additional metathesis reactions to further derivatize 9-decenoic acid was demonstrated in task 2e.

Completed work in Task 4 successfully addressed estimating physical properties, detailed reactor modeling, evaluating separation schemes, detailed process flowsheeting and mass balances, high-level economic modeling, and 100-lb 9DA production trial. Realization of the economic impact on ethenolysis conversion costs led to expanding the project to perform two scoping studies in the area of novel reactor design, reactive separation reactor design and high intensity reactor design. The pilot scale trial for the production of 9DA successfully demonstrated the scale-up of the ethenolysis chemistry and separation for pure 9DA. Production cost estimates for 9DA have been developed at the +100/-50% confidence level.

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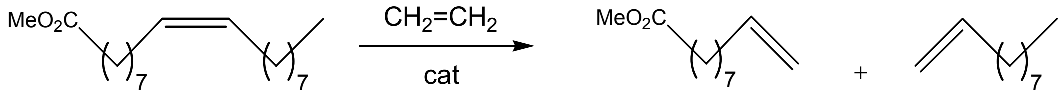
List of Appendices

Appendix A

The following abbreviations and definitions were used in the analysis of the ethenolysis of methyl oleate:



MO **MeO$_2$-9C$_{10}$** **1C$_{10}$**

MO: methyl oleate

cat: catalyst

MeO$_2$-9C$_{10}$: methyl-9-decenoate

1C$_{10}$: 1-decene

MO/cat: number of moles of methyl oleate divided by the number of moles of catalyst

Catalyst loading (ppm): number of moles of catalyst divided by number of moles of methyl oleate multiplied by 10^6

Catalyst loading (mol %): number of moles of catalyst divided by number of moles of methyl oleate multiplied by 100

Yield (%): sum of the percentages of ethenolysis products (MeO$_2$-9C$_{10}$ and 1C$_{10}$) as determined by gas chromatography (GC) analysis

Turnover Number or TON: MO/cat multiplied by Yield divided by 100

Turnover Frequency or TOF (h^{-1}): TON divided by reaction time

Appendix B

Procedure for low pressure (60-180psi) ethenolysis of pure methyl oleate: The experiments were set up under an atmosphere of argon in a glove box. Methyl oleate, > 99% (15.0 g; 50.6 mmoles) used as received from Nu-Check-Prep or purified by allowing to sit over activated alumina was charged in a Fisher-Porter bottle equipped with a stir bar. A solution of olefin metathesis catalyst of an appropriate concentration was prepared in dichloromethane and the desired volume of this solution added to the methyl oleate. The Fisher-Porter bottle's head equipped with a pressure gauge and a dip-tube was adapted on the bottle. The system was sealed and taken out of the glove box to the ethylene line. The vessel was then purged with ethylene (3 times), pressurized to the indicated pressure and placed in an oil bath at the indicated temperature. The reaction was monitored by collecting samples via the dip-tube at different reaction. Prior to GC analysis the reaction was quenched by adding a 1.0 M isopropanol solution of tris-hydroxymethylphopshine (THMP) to each vial over the course of 2-3 hours. The samples were then heated for at least 1 hour at 60°C, diluted with distilled water, extracted with hexanes and analyzed by GC.

Procedure for high pressure (200-1,000 psi) ethenolysis of pure methyl oleate: A procedure similar to that described above was used for high pressure ethenolyses except that a high pressure Paar reactor was used in place of the Fisher-Porter bottle.

Appendix C

Procedure for Gas Chromatography analysis: The products were analyzed by gas chromatography (GC) using a flame ionization detector (FID). The following conditions and equipment were used:

Column:	Rtx-5, 30m x 0.25mm (ID) x 0.25µm film thickness. Manufacturer: Restek
GC and column conditions:	Injector temperature: 250°C Detector temperature: 280°C
Oven temperature:	Starting temperature: 100°C, hold time: 1 minute. Ramp rate 10°C/min to 250°C, hold time: 12 minutes. Carrier gas: Helium
Mean gas velocity:	31.3 ± 3.5% cm/sec (calculated)
Split ratio:	~50:1

The products are characterized by comparing peaks with known standards, in conjunction with supporting data from mass spectrum analysis using a mass spectrum detector (GCMS-Agilent 5973N).

Table C1: Retention times (RT) for methyl oleate, ethenolysis products and possible impurities.

RT	Compound
2.23	1-Decene
2.33	E-2-Decene
2.40	Z-2-Decene
4.40	Methyl 8-Nonenoate
5.64	Methyl 9-Decenoate
5.79	Methyl E-8-Decenoate
5.94	Methyl Z-8-Decenoate
11.22	Z-9-Octadecene
11.29	E-9-Octadecene
14.69	Methyl Oleate
14.76	Methyl Elaidate
15.95	1, 16-Dimethyl Z-8-Hexadecenedioate
16.00	1, 16-Dimethyl E-8-Hexadecenedioate
18.11	1, 18-Dimethyl Z-9-Octadecenedioate
18.18	1, 18-Dimethyl E-9-Octadecenedioate

Appendix D

The reactors used for low pressure (60-180 psi) ethenolyses were designed and built at Materia (see Figure D1).

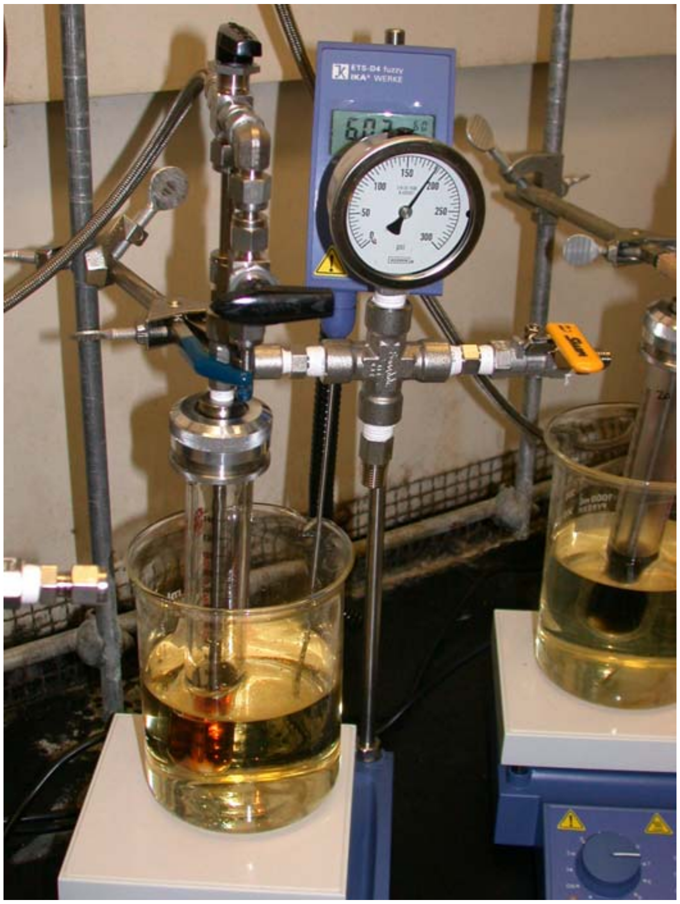
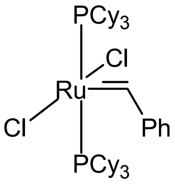
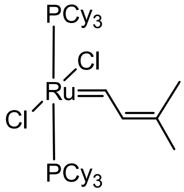


Figure D1: Low pressure (60-180 psi) ethenolysis reactor

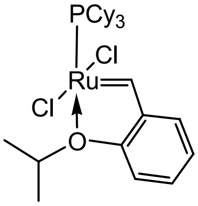
Appendix E



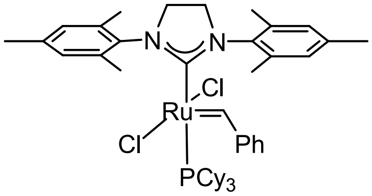
C823



C801



C601



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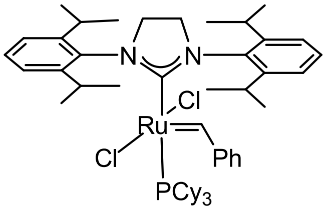

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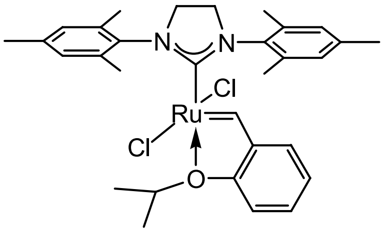
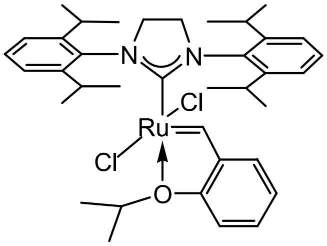


C627



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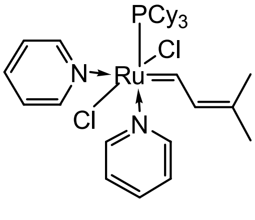
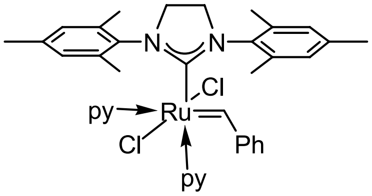


C679



C727

Figure E1: Drawings of catalysts tested in initial screens

Table F1: Ethenolysis of Research Grade Methyl Oleate Using C823.

Entry #	Note book #	Catalyst	MO/cat	Cat. loading (ppm)	P. (psig)	T. (°C)	Yield (%)	TON
1	068-008	C823	1,000	1,000	60	30	56	560
2	068-037	C823	1,000	1,000	120	30	77	770
3	068-018	C823	1,000	1,000	180	30	77	770
4	065-025	C823	1,000	1,000	360	30	50	500
5	068-030	C823	1,000	1,000	180	40	80	800
6	068-031	C823	1,000	1,000	180	50	75	750
7	068-019	C823	1,000	1,000	180	60	63	630
8	068-032	C823	1,000	1,000	180	70	60	600
9	068-010	C823	10,000	100	60	30	47	4,700
10	068-034	C823	10,000	100	180	30	69	6,900
11	065-025	C823	10,000	100	360	30	49	4,900
12	068-011	C823	100,000	10	60	30	9	9,000
13	068-035	C823	100,000	10	180	30	24	24,000
14	068-100	C823	100,000	10	180	25	19	19,000
15	068-101	C823	100,000	10	180	30	19	19,000
16	068-102	C823	100,000	10	180	35	19	19,000
17	068-103	C823	100,000	10	180	40	20	20,000
18	068-104	C823	100,000	10	120	40	25	25,000
19	068-105	C823	100,000	10	140	40	22	22,000
20	068-106	C823	100,000	10	160	40	25	25,000
21	068-107	C823	100,000	10	180	40	22	22,000
22	068-092	C823	100,000*	10	180	40	31	31,000
23	068-112	C823	28,600	35	120	40	45	13,000
24	068-108	C823	28,600*	35	120	40	45	13,000
25	068-113	C823	40,000	25	120	40	40	16,000
26	068-109	C823	40,000*	25	120	40	40	16,000
27	068-114	C823	67,500	15	120	40	34	23,000
28	068-110	C823	67,500*	15	120	40	39	26,000
29	068-115	C823	200,000	5	120	40	8	16,000
30	068-111	C823	200,000*	5	120	40	14	27,000
31	068-036	C823	1,000,000	1	180	30	0.3	3,000

- : Research grade methyl oleate was further purified by being left over activated alumina for at least 12 hours.

Table F2: Ethenolysis of Research Grade Methyl Oleate Using C801, C601 and C679.

Entry #	Note book #	Catalyst	MO/cat	Cat. loading (ppm)	P. (psig)	T. (ºC)	Yield (%)	TON
1	068-072	C801	1,000	1,000	180	20	66	660
2	068-073	C801	1,000	1,000	180	30	76	760
3	068-074	C801	1,000	1,000	180	40	71	710
4	065-075	C801	1,000	1,000	180	50	69	690
5	068-077	C801	10,000	100	180	30	58	5,800
6	068-078	C801	100,000	10	180	30	6	6,000
7	068-116	C801	28,600	35	120	40	31	9,000
8	068-120	C801	28600*	35	120	40	38	11,000
9	068-117	C801	40,000	25	120	40	28	11,000
10	068-121	C801	40,000*	25	120	40	52	13,000
11	065-118	C801	67,500	15	120	40	19	13,000
12	068-122	C801	67,500*	15	120	40	22	15,000
13	068-119	C801	200,000	5	120	40	4	8,000
14	068-123	C801	200,000*	5	120	40	9.5	19,000
15	068-020	C601	1,000	1,000	180	30	70	700
16	068-132	C601	100,000	10	120	40	25	25,000
17	068-133	C601	100,000	10	140	40	25	25,000
18	068-134	C601	100,000	10	160	40	26	26,000
19	068-135	C601	100,000	10	180	40	25	25,000
20	068-124	C601	28,600	35	120	40	35	10,000
21	068-128	C601	28,600*	35	120	40	38	11,000
22	068-125	C601	40,000	25	120	40	30	12,000
23	068-129	C601	40,000*	25	120	40	32.5	13,000
24	068-126	C601	67,500	15	120	40	28	16,000
25	068-130	C601	67,500*	15	120	40	28	19,000
26	068-127	C601	200,000	5	120	40	5.5	11,000
27	068-131	C601	200,000*	5	120	40	17	34,000
28	068-048	C679	1,000	1,000	180	30	3.5	35
29	068-055	C679 (solid)	1,000	1,000	180	30	26	260

- : Research grade methyl oleate was further purified by being left over activated alumina for at least 12 hours.

Table F3: Ethenolysis of research grade methyl oleate using second generation catalysts.

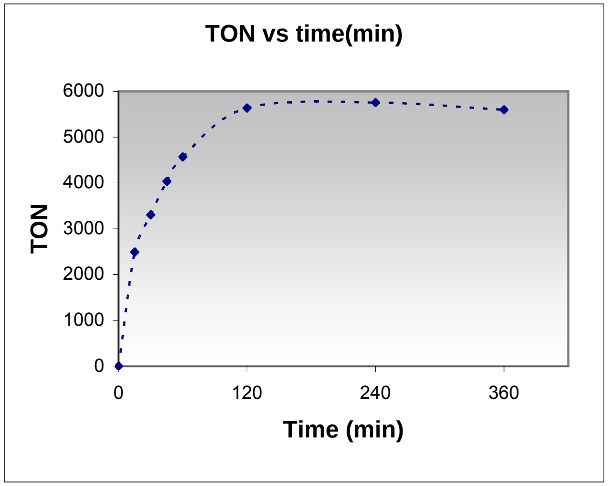
Entry #	Note book #	Solvent	MO/Solvent (v/v %)	Catalyst	MO/cat	P. (psig)	T. (°C)	Yield (%)	TON
1	068-007	none	N/A	848	1,000	60	20	7	70
2	065-021	none	N/A	848	1,000	500	20	4	40
3	068-006	none	N/A	848	1,000	60	60	30	300
4	068-015	none	N/A	848	1,000	180	60	41	410
5	068-014	none	N/A	848	1,000	180	30	25	250
6	068-022	toluene	50	848	1,000	180	30	30	300
7	068-023	toluene	25	848	1,000	180	30	32	320
8	068-024	toluene	10	848	1,000	180	30	17	170
9	068-025	toluene	5	848	1,000	180	30	13	130
10	065-021	none	N/A	627	1,000	500	20	15	150
11	068-016	none	N/A	627	1,000	180	30	35	350
12	068-026	toluene	50	627	1,000	180	30	41	410
13	068-027	toluene	25	627	1,000	180	30	32	320
14	068-028	toluene	10	627	1,000	180	30	30	300
15	068-029	toluene	5	627	1,000	180	30	22	220
16	068-039	none	N/A	727	1,000	180	30	8	80
17	068-043	none	N/A	712	1,000	180	30	60	600
18	068-044	none	N/A	712	10,000	180	30	47	4,700
19	068-045	none	N/A	712	100,000	180	30	7	7,000
20	068-052	none	N/A	933	1,000	180	30	43	430
21	068-053	none	N/A	933	10,000	180	30	38	3,800
22	068-054	none	N/A	933	100,000	180	30	25	25,000

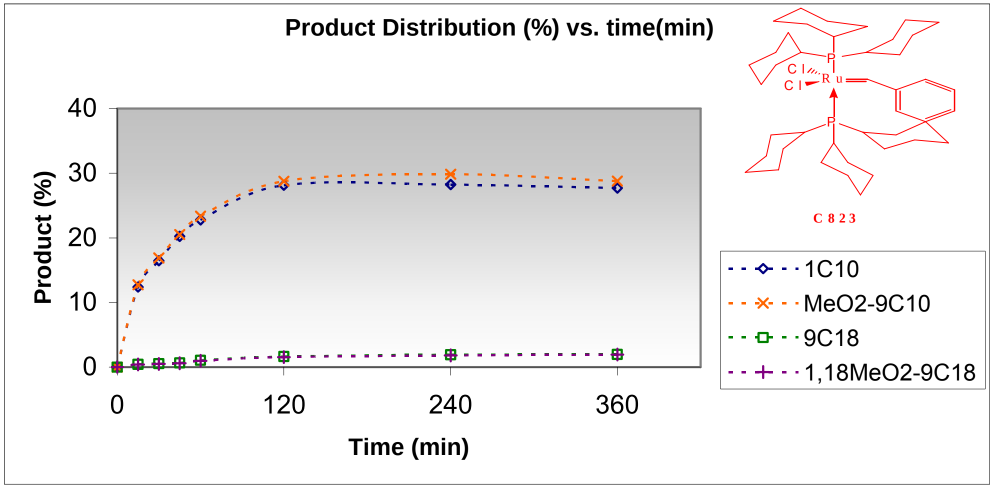
Ethenolysis of Research Grade Methyl Oleate(N.P.) filter through Alumina, in molecular sieves with C823 (0.01 mol %) at 40C and 150psig Ethylene

Note book #	Catalyst	Catalyst (mg)	Catalyst (mmoles)	MO (g)	MO (mmoles)	MO/cat	P. (psig)	T. (°C)
TU112-020	823	2.8	0.0034000	10	33.70	9910	150	40

Table 1

Sample #	Time (min.)	MO (%)	$1C_{10}$ (%)	MeO_2-$9C_{10}$ (%)	$9C_{18}$ (%)	1,18MeO_2-$9C_{18}$ (%)	Impurities (%)	Yield (%)	TON
0	0	100.00	0.00	0.00	0.00	0.00	0.00	0.00	-
112-020-40C	15	72.68	12.38	12.73	0.43	0.40	1.38	25.11	2,488
112-020-40C	30	63.84	16.45	16.89	0.53	0.50	1.79	33.34	3,304
112-020-40C	45	56.08	20.22	20.51	0.64	0.60	1.95	40.73	4,036
112-020-40C	60	49.82	22.78	23.34	1.05	0.97	2.04	46.12	4,570
112-020-40C	120	37.67	28.12	28.76	1.63	1.56	2.26	56.88	5,637
112-020-40C	240	31.70	28.24	29.83	1.93	1.81	6.49	58.07	5,755
112-020-40C	360	28.33	27.70	28.78	1.96	1.94	11.29	56.48	5,597



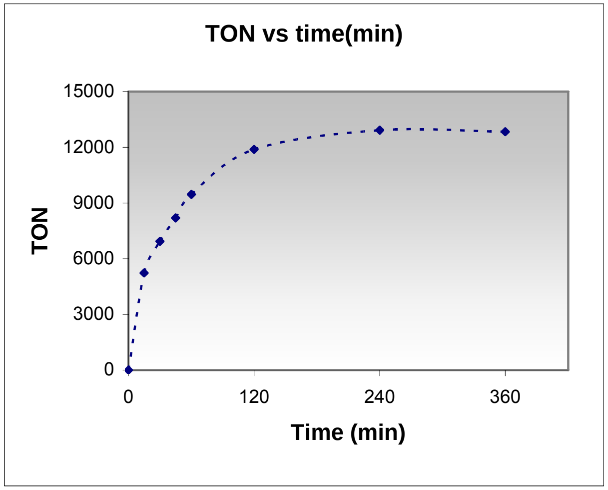


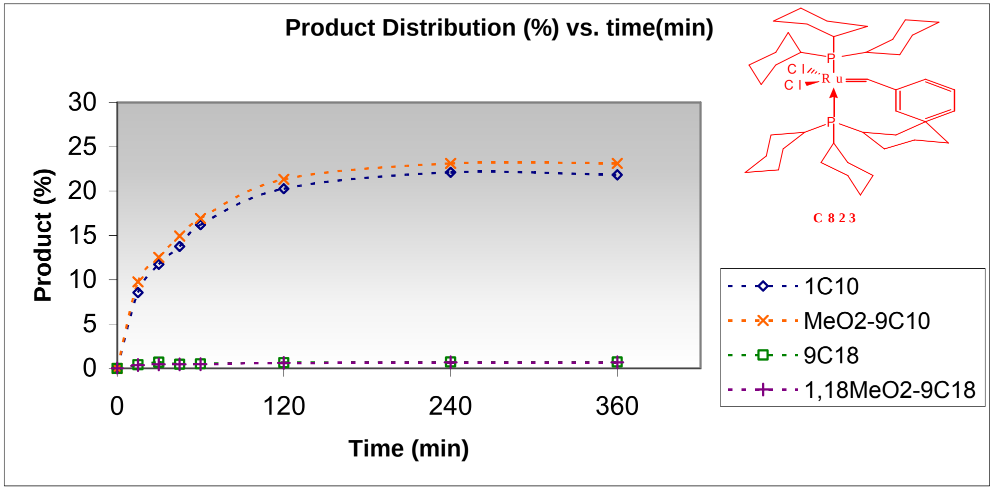
Ethenolysis of Research Grade Methyl Oleate(N.P.) in Alumina with C823 (0.0035 mol %) at 40C and 150psig Ethylene

Note book #	Catalyst	Catalyst (mg)	Catalyst (mmoles)	MO (g)	MO (mmoles)	MO/cat	P. (psig)	T. (°C)
TU112-024	823	0.97	0.0011800	10	33.70	28560	150	40

Table 1

Sample #	Time (min.)	MO (%)	1C$_{10}$ (%)	MeO$_2$-9C$_{10}$ (%)	9C$_{18}$ (%)	1,18MeO$_2$-9C$_{18}$ (%)	Impurities (%)	Yield (%)	TON
0	0	100.00	0.00	0.00	0.00	0.00	0.00	0.00	-
112-024-40C	15	80.87	8.56	9.76	0.41	0.38	0.02	18.32	5,232
112-024-40C	30	74.58	11.74	12.53	0.69	0.45	0.01	24.27	6,932
112-024-40C	45	70.38	13.76	14.93	0.47	0.45	0.01	28.69	8,194
112-024-40C	60	65.88	16.21	16.92	0.51	0.48	0.00	33.13	9,462
112-024-40C	120	57.14	20.28	21.33	0.64	0.61	0.00	41.61	11,884
112-024-40C	240	52.06	22.12	23.12	0.72	0.67	1.31	45.24	12,921
112-024-40C	360	51.86	21.84	23.13	0.73	0.68	1.76	44.97	12,843



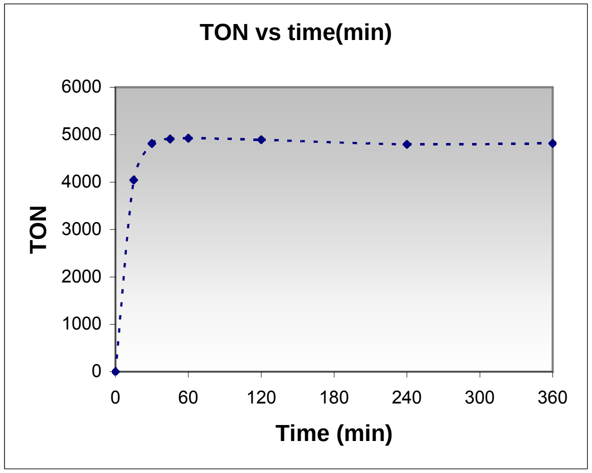


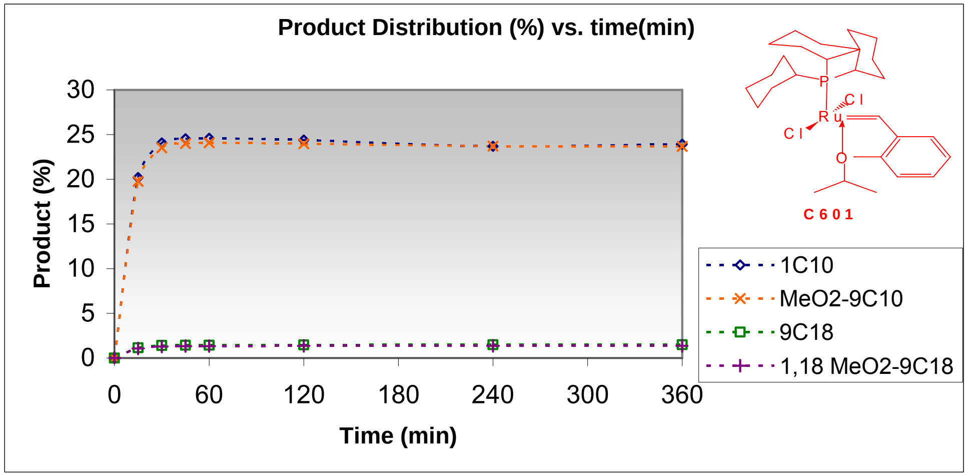
Ethenolysis of Research Grade Methyl Oleate(N.P.) in Alumina with C601 (0.01 mol %) at 40C and at 150psig Ethylene

Note book #	Catalyst	Catalyst (mg)	Catalyst (mmoles)	MO (g)	MO (mmoles)	MO/cat	P. (psig)	T. (°C)
75-159	601	2.0	0.0033300	10	33.70	10120	150	40

Table 1

Sample #	Time (min.)	MO (%)	1C$_{10}$ (%)	MeO$_2$-9C$_{10}$ (%)	9C$_{18}$ (%)	1,18MeO$_2$-9C$_{18}$ (%)	Impurities (%)	Yield (%)	TON
0	0	100.00	0.00	0.00	0.00	0.00	0.00	0.00	-
75-159-40C	15	57.68	20.19	19.75	1.14	1.06	0.18	39.94	4,042
75-159-40C	30	49.26	24.06	23.52	1.40	1.28	0.48	47.58	4,815
75-159-40C	45	48.02	24.52	23.99	1.43	1.33	0.71	48.51	4,909
75-159-40C	60	47.62	24.58	24.08	1.43	1.33	0.96	48.66	4,924
75-159-40C	120	47.27	24.38	23.98	1.46	1.35	1.56	48.36	4,894
75-159-40C	240	47.22	23.69	23.70	1.48	1.35	2.56	47.39	4,796
75-159-40C	360	46.78	23.92	23.67	1.47	1.35	2.81	47.59	4,816



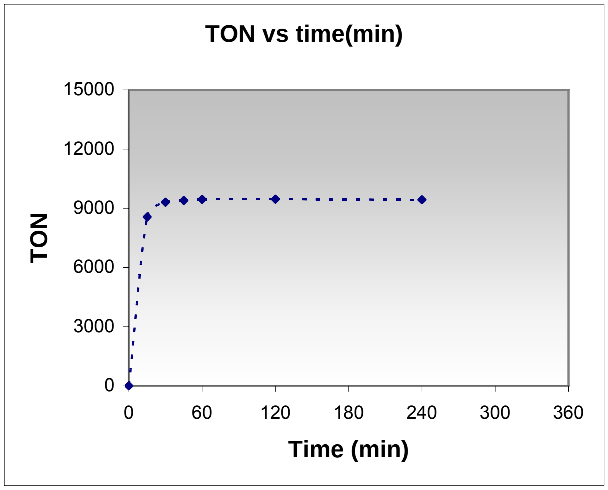


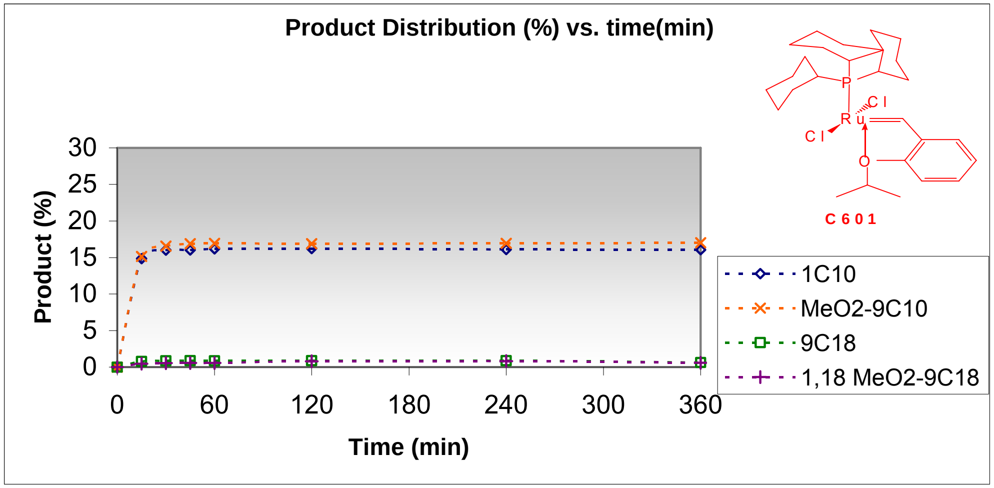
Ethenolysis of Research Grade Methyl Oleate(N.P.) in Alumina with C601 (0.0035mol %) at 40C and at 150psig Ethylene

Note book #	Catalyst	Catalyst (mg)	Catalyst (mmoles)	MO (g)	MO (mmoles)	MO/cat	P. (psig)	T. (°C)
112-029	601	0.71	0.0011800	10	33.70	28560	150	40

Table 1

Sample #	Time (min.)	MO (%)	$1C_{10}$ (%)	MeO_2-$9C_{10}$ (%)	$9C_{18}$ (%)	1,18MeO_2-$9C_{18}$ (%)	Impurities (%)	Yield (%)	TON
0	0	100.00	0.00	0.00	0.00	0.00	0.00	0.00	-
112-029-40C	15	68.75	14.83	15.14	0.79	0.48	0.01	29.97	8,559
112-029-40C	30	66.03	16.01	16.56	0.85	0.55	0.00	32.57	9,302
112-029-40C	45	65.64	16.02	16.88	0.88	0.58	0.00	32.90	9,396
112-029-40C	60	65.47	16.17	16.93	0.86	0.57	0.00	33.10	9,453
112-029-40C	120	65.02	16.24	16.88	0.88	0.80	0.18	33.12	9,459
112-029-40C	240	64.68	16.10	16.93	0.88	0.82	0.59	33.03	9,433
112-029-40C	360	65.71	16.06	17.01	0.63	0.59	0.00	33.07	9,445



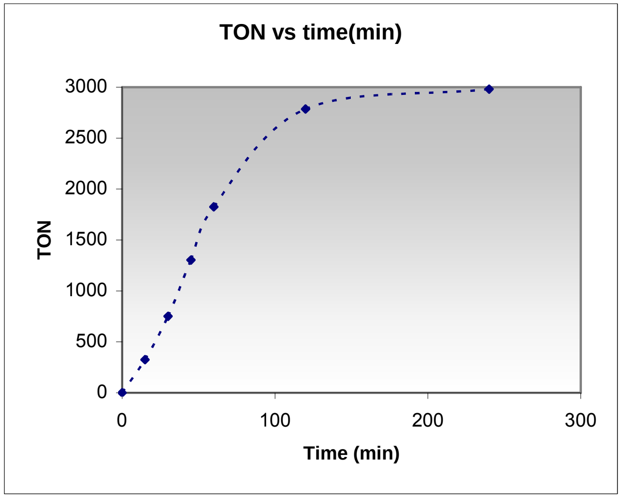


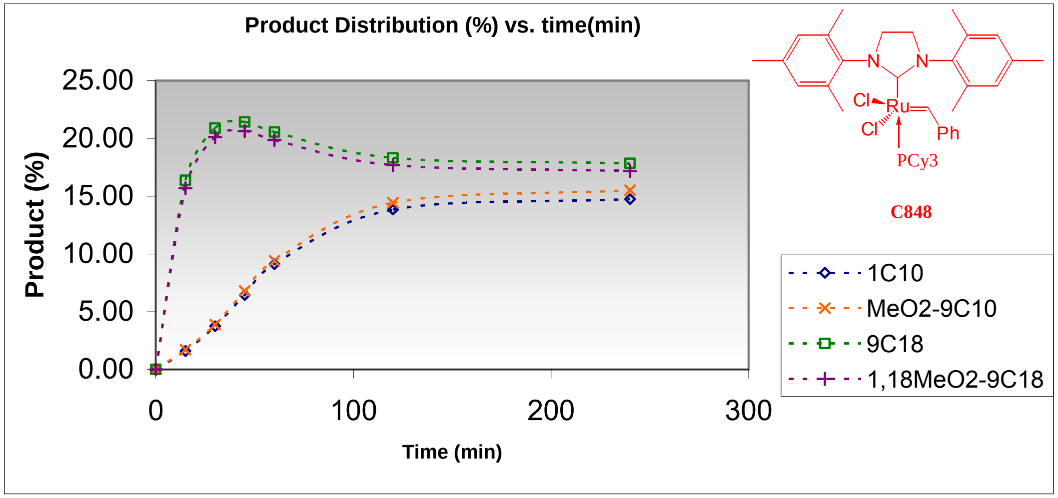
Ethenolysis of Research Grade Methyl Oleate(N.P.) in Alumina with C848(0.01 mol %) at 40C and 150 psi of Ethylene

Note book #	Catalyst	Catalyst (mg)	Catalyst (mmoles)	MO (g)	MO (mmoles)	MO/cat	P. (psig)	T. (°C)
TU-112-009	848	2.9	0.0034200	10	33.70	9850	150	40

Table 1

Sample #	Time (min)	MO (%)	1C_{10} (%)	MeO_2-9C_{10} (%)	9C_{18} (%)	1,18MeO_2-9C_{18} (%)	Impurities (%)	Yield (%)	TON
0	0	100.00	0.00	0.00	0.00	0.00	0.00	0.00	-
112-009	15	64.62	1.59	1.71	16.38	15.69	0.01	3.30	325
112-009	30	51.37	3.74	3.88	20.90	20.11	0.00	7.62	751
112-009	45	44.70	6.44	6.79	21.43	20.64	0.00	13.23	1,303
112-009	60	41.05	9.11	9.41	20.56	19.87	0.00	18.52	1,824
112-009	120	35.73	13.84	14.43	18.31	17.69	0.00	28.27	2,785
112-009	240	34.72	14.74	15.51	17.84	17.18	0.01	30.25	2,980



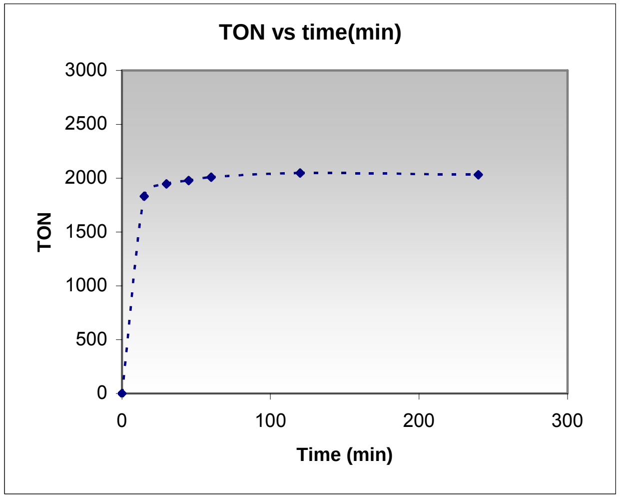


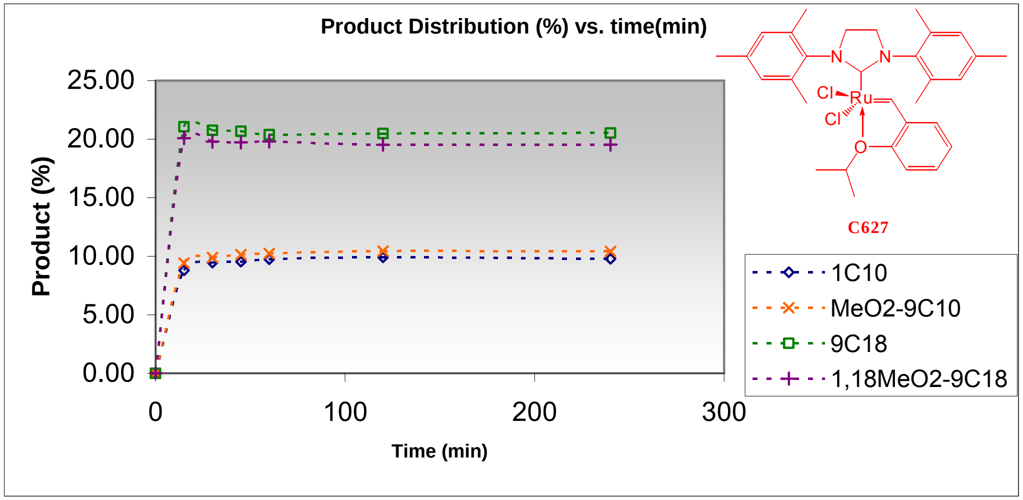
Ethenolysis of Research Grade Methyl Oleate(N.P.) in Alumina with C627(0.01 mol %) at 40C and 150 psi Ethylene.

Note book #	Catalyst	Catalyst (mg)	Catalyst (mmoles)	MO (g)	MO (mmoles)	MO/cat	P. (psig)	T. (°C)
TU-112-010	627	2.1	0.0033500	10	33.70	10060	150	40

Table 1

Sample #	Time (min)	MO (%)	1C$_{10}$ (%)	MeO$_2$-9C$_{10}$ (%)	9C$_{18}$ (%)	1,18MeO$_2$-9C$_{18}$ (%)	Impurities (%)	Yield (%)	TON
0	0	100.00	0.00	0.00	0.00	0.00	0.00	0.00	-
112-010	15	40.66	8.80	9.41	21.05	20.08	0.00	18.21	1,832
112-010	30	40.09	9.46	9.89	20.76	19.79	0.01	19.35	1,947
112-010	45	39.93	9.53	10.13	20.68	19.72	0.01	19.66	1,978
112-010	60	39.76	9.74	10.23	20.38	19.80	0.09	19.97	2,009
112-010	120	39.62	9.92	10.44	20.48	19.52	0.02	20.36	2,048
112-010	240	39.71	9.78	10.42	20.53	19.54	0.02	20.20	2,032



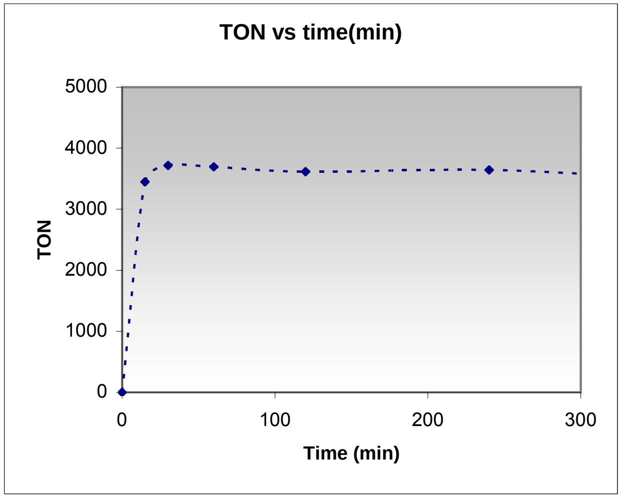


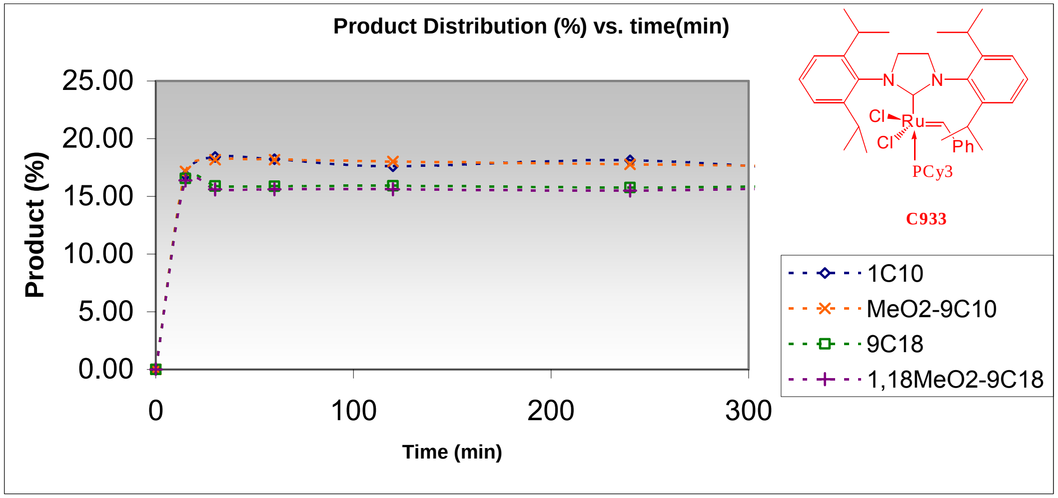
Ethenolysis of Research Grade Methyl Oleate(N.P.) in Alumina with C933(0.01 mol %) at 40C and 150 psi of Ethylene

Note book #	Catalyst	Catalyst (mg)	Catalyst (mmoles)	MO (g)	MO (mmoles)	MO/cat	P. (psig)	T. (°C)
TU-112-107	933	3.1	0.0033200	10	33.70	10150	150	40

Table 1

Sample #	Time (min)	MO (%)	$1C_{10}$ (%)	MeO_2-$9C_{10}$ (%)	$9C_{18}$ (%)	1,18MeO_2-$9C_{18}$ (%)	Impurities (%)	Yield (%)	TON
0	0	100.00	0.00	0.00	0.00	0.00	0.00	0.00	-
112-107	15	32.84	16.82	17.17	16.56	16.39	0.22	33.99	3,450
112-107	30	31.40	18.42	18.19	15.90	15.60	0.49	36.61	3,716
112-107	60	31.33	18.22	18.18	15.88	15.61	0.78	36.40	3,695
112-107	120	31.37	17.61	18.02	15.92	15.61	1.47	35.63	3,616
112-107	240	31.15	18.12	17.77	15.76	15.51	1.69	35.89	3,643
112-107	360	31.90	16.93	17.54	15.97	15.83	1.83	34.47	3,499



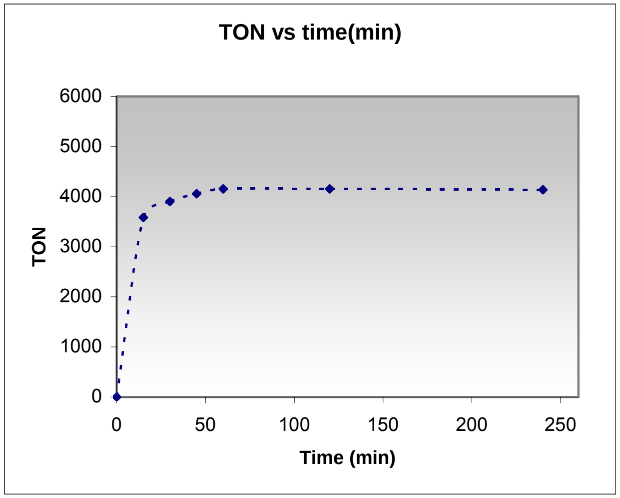


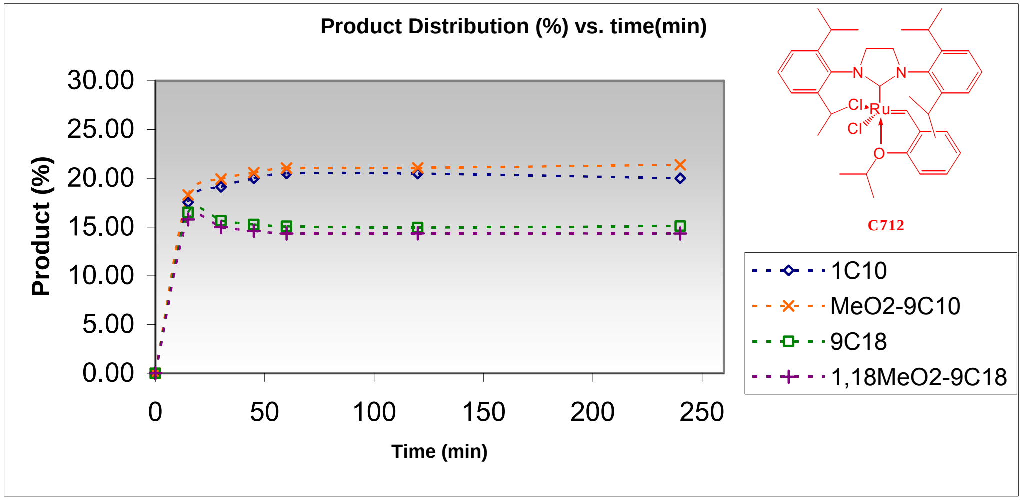
Ethenolysis of Research Grade Methyl Oleate(N.P.) in Alumina with C712(0.01 mol %) at 40C and 150psi Ethylene

Note book #	Catalyst	Catalyst (mg)	Catalyst (mmoles)	MO (g)	MO (mmoles)	MO/cat	P. (psig)	T. (ºC)
TU112-015	712	2.4	0.0033700	10	33.70	10000	150	40

Table 1

Sample #	Time (min)	MO (%)	$1C_{10}$ (%)	MeO_2-$9C_{10}$ (%)	$9C_{18}$ (%)	1,18MeO_2-$9C_{18}$ (%)	Impurities (%)	Yield (%)	TON
0	0	100.00	0.00	0.00	0.00	0.00	0.00	0.00	-
112-015	15	31.90	17.55	18.29	16.49	15.77	0.00	35.84	3,584
112-015	30	30.36	19.11	19.90	15.65	14.98	0.00	39.01	3,901
112-015	45	29.57	19.99	20.57	15.26	14.61	0.00	40.56	4,056
112-015	60	29.07	20.50	21.04	15.06	14.33	0.00	41.54	4,154
112-015	120	29.15	20.48	21.07	14.95	14.35	0.00	41.55	4,155
112-015	240	29.21	19.99	21.38	15.09	14.33	0.00	41.37	4,137





Appendix H

Procedure for treatment of technical grade methyl oleate: Technical grade methyl oleate was optionally purified by filtration through activated alumina: the alumina was activated for 1-2 hours at 200°C in a convection oven then cooled to room temperature under full vacuum. The activated alumina was then placed in a 3-L glass funnel with a coarse frit (1 g of alumina for 3 g of methyl oleate), methyl oleate poured into the funnel and allowed to drain into a flask containing sufficient BHT to achieve a 25 ppm concentration. The filtered product was sparged for 15 minutes with argon, bottled, and stored in a freezer if not used immediately.

Procedure for ethenolysis of technical grade methyl oleate: The ethenolyses of technical grade methyl oleate were run in a 2 L stainless steel Parr reactor, which was pre-heated to about 40 °C. The methyl oleate was charged and sparged for 5 minutes with argon. The reactor was then sealed and pressurized to 40 psi with argon, then vented and pressurized again to 40 psi and the methyl oleate warmed to 40 °C while stirring at 350 rpm. The reactor was vented, opened, and the catalyst was added. The reactor was closed, pressurized to 40 psi with argon, and vented. This operation was repeated twice before pressurizing the reactor to 180 psi with 99.9% ethylene. The pressure was then released and the operation repeated 3 times with ethylene. The ethylene pressure was maintained at 180 psi for the duration of the reaction. The reaction mixture was kept at 40 °C and stirred at 350 rpm for 2 to 6 hours. The pressure was then released and the reactor pressurized to 40 psi with argon and then bled down to purge residual ethylene. A 1.0 M solution of THMP in isopropanol was added to the reaction mixture (at least 20 fold molar excess with respect to the catalyst), before it was heated to 60-80 °C with stirring for 2-15 hours. Water (200 mL) was added and the mixture washed by stirring for 10 minutes. The mixture was placed in a separatory funnel and the layers are allowed to separate. The aqueous layer was drained and the organic layer washed 2 more times with water (200 mL). The organic layer was dried with sodium sulfate for several hours, then filtered and bottled for later distillation.

Purification of methyl 9-decenoate: Methyl 9-decenoate, from ethenolysis reactions, was purified to ~90% by short path vacuum distillation. High purity methyl 9-decenoate was produced by using a 2 inch x 36 inch packed distillation column containing 0.16 inch 316SS Pro-Pak^{TM} (protruded metal distillation packing from Cannon Instruments, State College, PA). Methyl 9-decenoate (190 g of ~90 % purity) was distilled (Bp 45°C to 49°C at 0.3 to 0.6 mmHg) to yield 120 g in 98.7 % purity.

Table H1: Ethenolysis of technical grade methyl oleate using C823

Entry #	Note book #	MO source	MO/cat	Purification	Yield (%)	TON
1	0'71-002	Aldrich	100	yes	64	64
2	071-004	Cognis	100	yes	62	62
3	0'71-005	Cognis	1,000	no	56	560
4	0'71-006	Cognis	1,000	yes	64	640
5	0'71-007	Cognis	10,000	yes	20	2,000
6	071-008	Cognis	2,000	yes	52	1,040
7	0'71-010	Nu-Chek Prep	10,000	yes	36	3,600
8	071-011	Nu-Chek Prep	2,000	yes	67	1,340

Appendix I

Table I1: Ethenolysis of different FAMEs using C823 (at 40 °C for 6 hours)

Entry #	Note book #	Oil	Source	Loading[f]	P. (psig)	Yield (%)[g]
1	90-035A	Soy FAME	Chemol Inc.	66	150	16
2	90-035B	Soy FAME	Chemol Inc.	350	150	32
3	90-035C	Soy FAME[a]	Chemol Inc.	66	150	32
4	90-035D	Soy FAME[a]	Chemol Inc.	350	150	48
5	90-037A	Soy FAME[b]	Chemol Inc.	66	150	8
6	90-037B	Soy FAME[b]	Chemol Inc.	350	150	22
7	90-037C	Soy FAME[a,b]	Chemol Inc.	66	150	26
8	90-037D	Soy FAME[a,b]	Chemol Inc.	350	150	48
9	90-041A	Canola FAME[c]	Materia	75	150	8
10	90-041B	Canola FAME[c]	Materia	350	150	42
11	90-045	Canola FAME[a,c]	Materia	75	150	32
12	90-041B	Canola FAME[a,c]	Materia	350	150	44
13	90-052	Canola FAME	Chemol inc.	75	150	18
14	90-053D	Canola FAME[a]	Chemol inc.	350	150	28
15	90-056A	Canola FAME[a]	Chemol inc.	75	150	1
16	90-056B	Canola FAME[a]	Chemol inc.	150	150	8
17	90-057A	Canola FAME[d]	Chemol inc.	75	150	1
18	90-057B	Canola FAME[d]	Chemol inc.	350	150	22
19	90-058A	Canola FAME[c]	Chemol inc.	75	150	20
20	90-058B	Canola FAME[e]	Chemol inc.	75	150	1
21	90-058C	Canola FAME[a,c]	Chemol inc.	75	150	30

a): treated with activated alumina; b): filtered through clay; c): trans-esterified and distilled; d): filtered through silica gel; e) heated at 60 °C under vacuum; f) The loadings are given in ppm of catalyst per double bond of substrate; g) The yields were approximated by doubling the GC area % of methyl 9-decenoate.

Appendix J

Table J1: Ethenolysis of different triacylglycerides

Entry #	Note book #	Oil	Source	Catalyst	Loading[g]	P. (psig)	Yield (%)[h]
1[a]	90-003B	Soybean oil	Cargill	C823	110	150	24
2[a]	90-001	Soybean oil	Cargill	C823	220	150	34
3[a]	90-003A	Soybean oil	Cargill	C823	440	150	39
4[a]	90-005A	Soybean oil	Cargill	C601	110	150	20
5[a]	90-005B	Soybean oil	Cargill	C601	220	150	26
6[a]	90-005C	Soybean oil	Cargill	C601	440	150	36
7[b]	90-015A	Soybean oil	Cargill	C627	110	150	14
8[b]	90-015B	Soybean oil	Cargill	C627	220	150	20
9[b]	90-017A	Soybean oil	Cargill	C712	20	150	22
10[b]	90-017B	Soybean oil	Cargill	C712	55	150	26
11[b]	90-017C	Soybean oil	Cargill	C712	110	150	30
12[b]	90-017D	Soybean oil	Cargill	C712	220	150	34
13[b]	90-044A	Soybean oil	Supermarket	C823	110	150	32
14[b]	90-044B	Soybean oil	Supermarket	C823	220	150	40
15[b]	90-047A	Soybean oil[c]	Supermarket	C823	110	150	36
16[b]	90-047B	Soybean oil[c]	Supermarket	C823	220	150	50
17[b]	90-048A	Soybean oil[c]	Cargill	C823	110	150	32
18[b]	90-048B	Soybean oil[c]	Cargill	C823	220	150	38
19[d]	90-091A	Soybean oil	Cargill	C712	110	900	32
20[e]	90-091B	Soybean oil	Cargill	C712	110	900	28
21[f]	90-091C	Soybean oil	Cargill	C712	110	900	40
22[d]	90-066D	Soybean oil	Cargill	C712	22	900	8
23[f]	90-115	Soybean oil	Cargill	C712	110	900	50
24[b]	90-043A	Canola oil	Supermarket	C823	110	150	30
25[b]	90-043B	Canola oil	Supermarket	C823	220	150	36
26[b]	90-074A	Canola oil	Cargill	C823	110	150	28
27[b]	90-074B	Canola oil	Cargill	C823	220	150	36
28[b]	90-075A	Peanut oil	Cargill	C823	110	150	14
29[b]	90-075B	Peanut oil	Cargill	C823	220	150	18
30[b]	90-087C	Palm oil	Cargill	C823	110	150	12
31[b]	90-087D	Palm oil	Cargill	C823	220	150	14
32[b]	90-090A	Linseed oil	Cargill	C823	110	150	16
33[b]	90-090B	Linseed oil	Cargill	C823	220	150	26
34[b]	90-090C	Sunflower oil	Cargill	C823	110	150	12
35[b]	90-090D	Sunflower oil	Cargill	C823	220	150	14

a): 2 hours at 40 °C; b): 6 hours at 40 °C; c): trans treated with activated alumina; d): 4 hours at 45 °C; e) 2 hours at 25 °C; f) 2 hours at 30 °C; g) The loadings are given in ppm of catalyst per double bond of substrate; h) The yields were approximated by doubling the GC area % of methyl 9-decenoate.

Appendix L

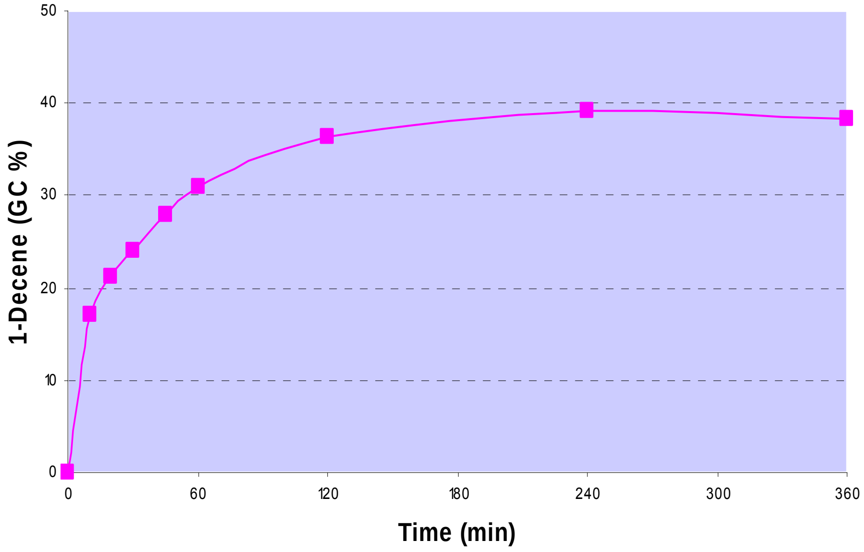


Figure L1: Ethenolysis of E-9-octadecene using C823 (100 ppm; 150 psi ethylene; 40 °C)

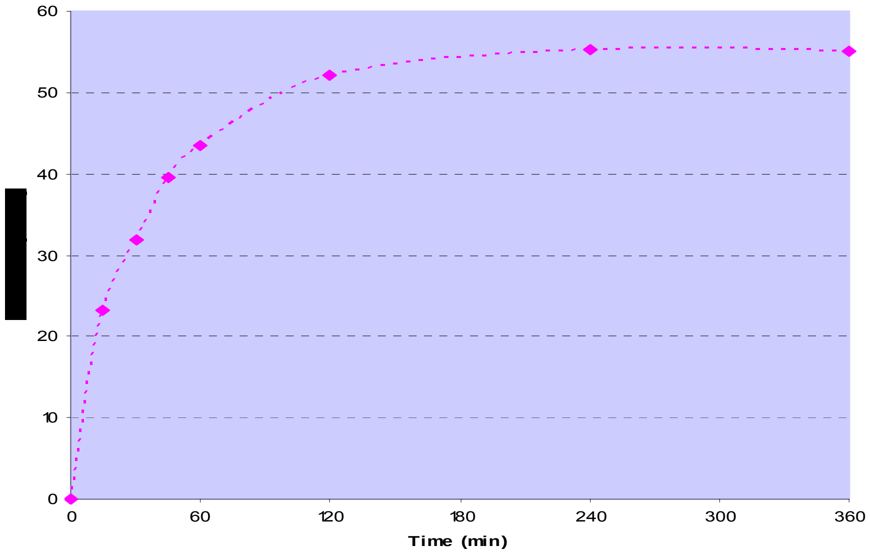
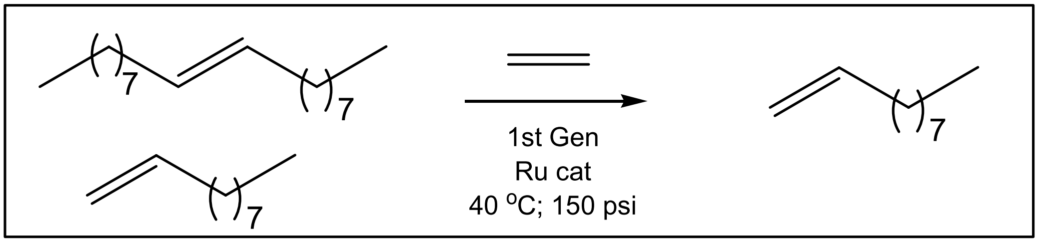


Figure L2: Ethenolysis of Z-9-octadecene using C823 (100 ppm; 150 psi ethylene; 40 °C)

Appendix M



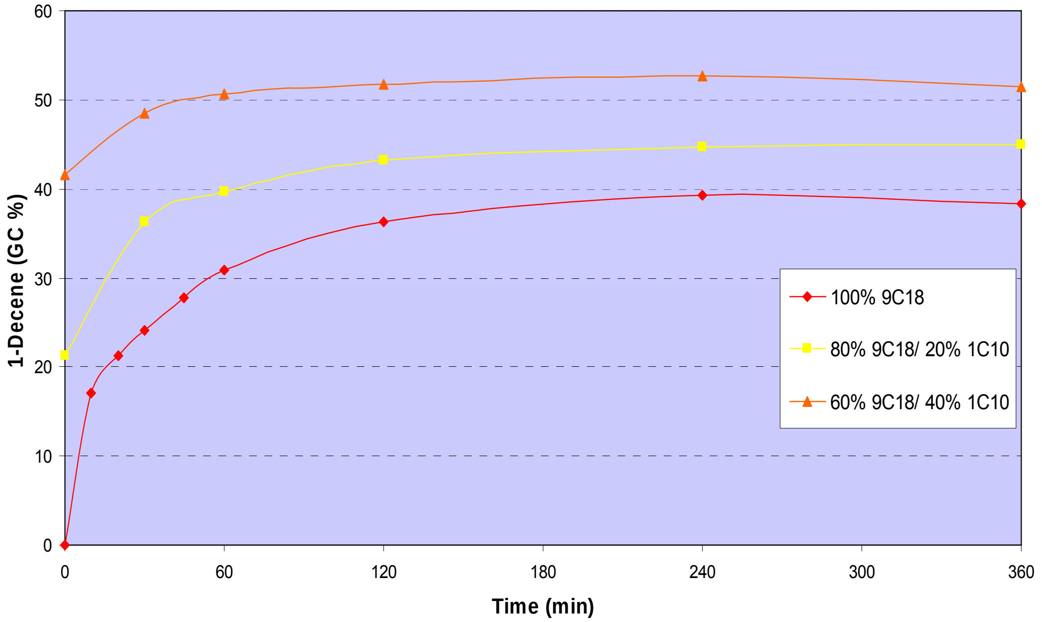
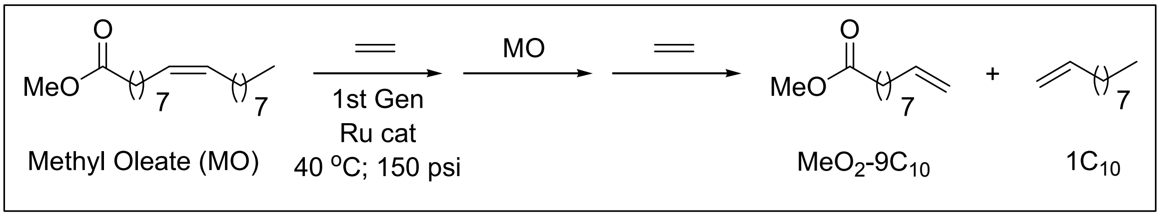


Figure M1: Ethenolysis of E-9-octadecene/1-decene mixtures (C823; 100 ppm; 150 psi ethylene; 40 °C)

Appendix N



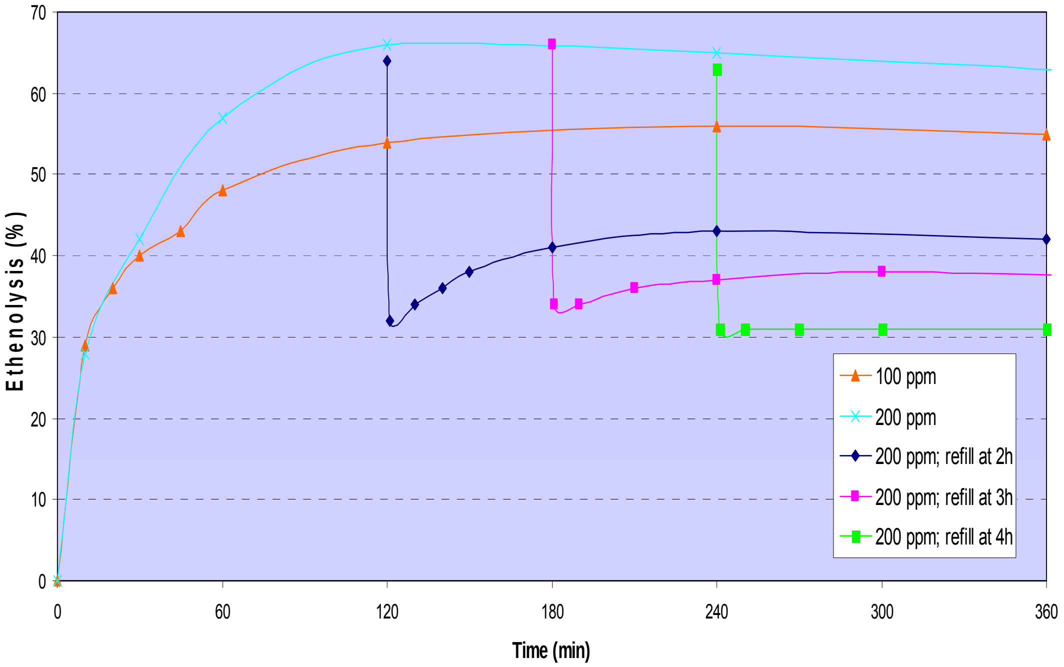


Figure N1: Ethenolysis of methyl oleate followed by addition of an equal volume of methyl oleate (C823; 100 ppm; 150 psi ethylene; 40 °C)

Appendix O

Procedure for studies of catalyst decomposition under ^{13}C-labeled ethylene: A J. Young tube was charged with a catalyst solution in CD_2Cl_2 or C_6D_6 in an argon-filled glovebox. The tube was sealed, brought out of the glovebox and connected to a vacuum line and a Strauss flask containing $^{13}CH_2{}^{13}CH_2$ by means of a three-way AirFree adaptor. The J. Young tube was then degassed by three freeze-pump-thaw cycles, evacuated to 30 mTorr while being cooled with liquid nitrogen and opened to the Strauss flask. Ethylene was allowed to condense in the J. Young tube for several seconds, after which the tube was sealed and brought to r.t. The reaction mixture was analyzed by ^{1}H, ^{13}C and ^{31}P NMR (when applicable) during the course of 24-30 h.

Procedure for studies of Grubbs-Hoveyda catalyst decomposition (1 atm ethylene): In a glovebox, the catalyst and Ph_2CH_2 (internal standard) were weight into a volumetric flask which was then filled with C_6D_6 to make a homogeneous solution. An NMR sample of this solution was set aside; the rest was placed into a vial equipped with a stirbar and an open-top septum-cap. The vial was sealed, brought out of the glovebox, evacuated to about 30 mTorr while being cooled with liquid nitrogen, then filled with 1 atm of ethylene and heated at 40 ^{o}C with stirring. Aliquots (about 1 mL) were withdrawn through the septum by means of a syringe, then immediately injected into vials containing a solution of trycyclohexylphosphine in C_6D_6 under argon. The quenched aliquots were then flushed with argon and frozen in liquid nitrogen. When several samples were collected (usually over 100-200 min), they were brought into a glovebox, thawed and placed into NMR tubes. The samples (including the original, undecomposed catalyst solution) were analyzed by ^{1}H NMR using careful integration of all Ru-alkylidene signals (15-25 ppm) and methylidene group of Ph2CH2 (3.7 ppm, 2H). The total integration value for all Ru-alkylidene signals was converted into concentration and this concentration was plotted as a function of reaction time. This procedure was also used for the reaction involving 1-hexene (14 equiv with respect to C601) which was used instead of ethylene.

Procedure for studies of Grubbs-Hoveyda catalyst decomposition (150 psi ethylene): In a glovebox, the catalyst and Ph_2CH_2 (internal standard) were weight into a volumetric flask which was then filled with C_6D_6 to make a homogeneous solution. An NMR sample of this solution was set aside; the rest was placed into Fisher-Porter vessel equipped with a stirbar and sampling tube connecter to a syringe with a 16-gauge needle. The Fisher-Porter bottle was sealed, brought out of the glovebox, flushed three times with ethylene, then pressurized with ethylene to about 150 psi and heated at 40 ^{o}C with stirring. Aliquots (about 1 mL) were withdrawn through the sampling tube directly into sealed, open-top, septum-capped vials containing a solution of trycyclohexylphosphine in C_6D_6 under argon. The quenched aliquots were then flushed with argon and frozen in liquid nitrogen. When several samples were collected (usually over 100-200 min), they were brought into a glovebox, thawed and placed into NMR tubes. The samples (including the original, undecomposed catalyst solution) were analyzed by ^{1}H NMR using careful integration of all Ru-alkylidene signals (15-25 ppm) and methylidene group of Ph2CH2 (3.7 ppm, 2H). The total integration value for all Ru-alkylidene signals was converted into concentration and this concentration was plotted as a function of reaction time.

Appendix R

Table R1: Ethenolysis of technical grade methyl oleate using C823 in the presence of various additives[a]

Entry	Notebook #	Additive	Equiv . of add.	Yield %
1	068-161	None	N/A	48 %
2	068-165	Pyridine	1	7 %
3	068-166	Pyridine	5	1 %
4	068-167	Pyridine	10	1 %
5	068-169	AcOH	1	45 %
6	068-170	AcOH	5	50 %
7	068-171	AcOH	10	50 %
8	068-173	HCl	1	44 %
9	068-174	HCl	5	53 %
10	068-175	HCl	10	54 %
11	068-181	CuCl	1	25 %
12	068-182	CuCl	5	22 %
13	068-183	CuCl	10	17 %
14	068-177	$Al(O\text{-}iPr)_3$	1	43 %
15	068-178	$Al(O\text{-}iPr)_3$	5	43 %
16	068-179	$Al(O\text{-}iPr)_3$	10	41 %
17	068-185	MAO	1	40 %
18	068-186	MAO	5	30 %
19	068-187	MAO	10	32 %
20	068-189	BHT	1	55 %
21	068-190	BHT	5	51 %
22	068-191	BHT	10	52 %

[a] General conditions: neat MO, 40 °C, 180 psi ethylene, catalyst loading = 100 ppm

Appendix S

Table S1: Comparison of 1st and 2nd generation catalysts in ethenolysis of MO.[a]

Entry	Catalyst	Temp (ºC)	Time (min)	Conversion (%)[b]	Selectivity (%)[c]	Yield (%)[d]	TON[e]	TOF (min^{-1})[f]
1	C823	40	120	58	93	54	5,400	45
2	C823	60	30	54	89	48	4,800	160
3	C601	40	30	51	94	48	4,800	160
4	C848	40	120	64	44	28	2,800	23
5	C848	60	<15	64	44	28	2,800	>190
6	C627	40	30	60	33	20	2,000	67
7	C627	60	<15	68	47	32	3,200	>210

[a] General conditions: neat MO, 150 psi ethylene, catalyst loading = 100 ppm

[b] Conversion = 100 – [(final moles of MO)*100/(initial moles of MO)]

[c] Selectivity = (moles of ethenolysis products)*100/(moles of total products)

[d] Yield = (moles of ethenolysis products)*100/(initial moles of MO) = Conversion*Selectivity/100

[e] TON = Yield*[(moles of MO)/(moles of Cat.)]

[f] TOF = TON/Time

Table S2: Comparison of different catalysts in the ethenolysis of MO

Entry	Cat.	Loading (ppm)	Time (min)	Conversion (%)	Selectivity (%)	Yield (%)	TON	TOF (min^{-1})
1[a]	C848	100	120	64	44	28	2,800	23
2[b]	C848	100	<15	64	44	28	2,800	>190
3[a]	C627	100	30	60	33	20	2,000	67
4[b]	C627	100	<15	68	47	32	3,200	>210
5[a]	C782	100	<15	38	71	27	2,700	>180
6[b]	C782	100	<15	53	60	32	3,200	>210
7[a]	C712	100	30	70	56	39	3,900	130
8[b]	C712	100	<15	79	71	56	5,600	>373
9[a]	C712	35	<15	69	57	39	11,000	>733
10[c]	C712	100	360	87	80	70	7,000	19
11[c]	C712	25	360	51	63	32	12,800	36
12[a]	C933	100	60	69	55	38	3,800	63
13[a]	C933	10	60	61	36	22	22,000	367
14[a]	C866	100	30	49	94	46	4,600	150
15[b]	C866	100	<15	43	88	38	3,800	>250
16[c]	C866	100	<30	39	92	36	3,600	>120
17[c]	C866	500	<15	86	94	81	1,620	>110
18[d]	C697	100	1260	66	53	35	3,560	<3
19[e]	C697	100	390	79	72	57	5,710	15
20[f]	C697	100	120	81	67	54	5,410	45
21[a]	C785	100	1380	58	55	32	3,200	<3
22[b]	C785	100	180	78	73	57	5,640	31
23[b]	C859	100	240	77	66	51	5,200	22
24[g]	C859	100	30	76	61	46	4,680	156
25[a]	C859	100	1200	71	59	42	4,200	<4

Entry	Cat.	Loading (ppm)	Time (min)	Conversion (%)	Selectivity (%)	Yield (%)	TON	TOF (min^{-1})
26[a]	C879	100	390	51	69	35	3,570	9
27[b]	C879	100	240	59	90	53	5,370	22
28[b]	C965-p	100	30	58	45	26	2,500	84
29[b]	C824	100	30	35	86	30	2,990	100
30[a]	C606	100	1,320	61	92	56	5,600	4
31[a]	C606	50	1,200	61	93	57	11,400	10
32[a]	C578	100	<30	73	73	53	5,300	>177
33[a]	C578	35	60	75	75	56	16,000	267
34[a]	C578	10	<30	42	83	35	35,000	>1,167
35[a]	C646	100	360	46	94	43	4,200	12
36[a]	C838	100	1320	60	90	54	5,440	4
37[g]	C577	100	300	74	84	62	6,330	21
38[b]	C577	100	1380	67	90	60	6,150	<5
39[a]	C767-m	100	30	37	32	12	1,150	38
40[a]	C811	100	15	62	34	21	2,100	140
41[a]	C916	100	15	65	45	29	2,900	194
42[b]	C827	100	120	75	64	48	4,790	40

[a] neat MO; 40 °C; 150 psi ethylene. [b] neat MO; 60 °C; 150 psi ethylene. [c] neat MO; 25 °C; 800 psi ethylene. [d] neat MO; 40 °C; 180 psi ethylene. [e] neat MO; 60 °C; 180 psi ethylene. [f] neat MO; 80 °C; 180 psi ethylene. [g] neat MO; 80 °C; 150 psi ethylene

Table S3: Comparison of C606 and C578 to C848 and C627 in ethenolysis of MO[a]

Entry	Cat.	Loading (ppm)	Time (min)	Conversion (%)	Selectivity (%)	Yield (%)	TON	TOF (min^{-1})
1	C848	100	120	64	44	28	2,800	23
2	C627	100	30	60	33	20	2,000	67
3	C606	100	1,320	61	92	56	5,600	4
4	C606	50	1,200	61	93	57	11,400	10
5	C578	100	<30	73	73	53	5,300	>177
6	C578	35	60	75	75	56	16,000	267
7	C578	10	<30	42	83	35	35,000	>1,167

[a] Conditions: neat MO; 40 °C; 150 psi ethylene.

Appendix T

Table T1: Ethenolysis of methyl oleate using C823 (0.1 mol %)

Ethenolysis of MO with Ru-823 (0.1mol%), rt								
Cat (0.1mol%)	**Pressure**	**Time(h)**	**%SM**	**% Yield**	**% Dimer**	**% Imp.**	**M/D**	**TON**
823	30	2	29	65	5	1	13	650
823	70	2	18	75	7	0	11	750
823	70	16	10	81	7	2	12	810
823	200	2	25	72	2	0	36	720
823	200	16	16	81	2	1	41	810
823	800	2	43	55	1	0	55	550
823	800	16	35	64	1	0	64	640

Table T2: Ethenolysis of methyl oleate using C823 (0.01 mol %)

Ethenolysis of MO with Ru-823 (0.01mol%), rt								
Cat (0.01mol%)	**Pressure**	**Time(h)**	**%SM**	**% Yield**	**% Dimer**	**% Imp.**	**M/D**	**TON**
823	30	2	60	39	1	0	39	3900
823	70	2	57	41	1	0	41	4100
823	70	16	35	62	1	1	62	6200
823	200	2	59	41	0	0	NA	4100
823	200	16	44	53	1	1	53	5300
823	800	2	64	36	0	0	NA	3600
823	800	16	49	51	0	0	NA	5100

Appendix U

Table U1: Ethenolysis of Methyl Oleate Using Second Generation Catalysts (0.01 mol%).

Ethenolysis of MO with Ru-2nd generation catalysts (0.01mol%), rt.								
Cat (0.01mol%)	**Pressure**	**Time(h)**	**%SM**	**% Yield**	**% Dimer**	**% Imp.**	**M/D**	**TON**
627	70	16	64	4	32	0	0.1	120
848	70	16	92	1	7	0	0.1	100
933	70	2	46	10	44	0	0.2	1000
933	70	16	48	4	48	0	0.1	400
933	200	2	63	4	33	0	0.1	400
933	800	2	55	17	28	0	0.6	1700
933	800	16	48	21	31	0	0.7	2100
712	70	2	31	38	31	0	1.2	3800
712	70	16	30	40	30	0	1.3	4000
712	200	2	33	39	28	0	1.4	3900
712	200	16	20	59	21	0	2.8	5900
712	800	16	14	75	9	1	8.3	7500
712	800	2	28	60	12	0	5	6000