

# Rhenium Oxide based Olefin Metathesis

Ryan F. Morrison, Nick Lipscomb, and R. Bruce Eldridge\*

Process Science and Technology Center, The University of Texas at Austin, Austin, Texas 78712, United States

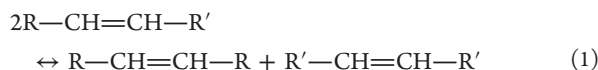
Peter Ginn

MPM Technology LP, 2525 Independence Parkway, Deer Park, Texas 77536-1914, United States

**ABSTRACT:** In support of a reactive distillation experimental program, bench scale experiments were conducted for the production of high molecular weight olefins via metathesis. A fixed bed rhenium oxide ( $\text{Re}_2\text{O}_7$ ) catalyst on a  $\gamma$ -alumina support was utilized to study the reaction of  $\text{C}_6$ ,  $\text{C}_8$ , and  $\text{C}_{10}$  olefins to form light and heavy olefin products. Initial experiments determined the impact temperature and weight hourly space velocity (WHSV) had on the reactivity of three different  $\alpha$ -olefins. The investigated temperatures and WHSV were conditions that encompassed the anticipated reactive distillation column reactor zones temperatures and WHSV. All of these runs displayed high conversions, low selectivities, and significant secondary isomerization coupled with subsequent metathesis. This isomerization compromised the ability to make any quantitative assessments on the reactivity of olefins with respect to temperature, flow rate, and carbon number in the feed. However, it was concluded that there was a possible optimal condition of a low flow and low temperature. Additional experiments revealed the impact temperature had on conversion and selectivity of  $\text{C}_8$  and  $\text{C}_{10}$   $\alpha$ -olefins. These experiments concluded that between an ambient temperature condition and  $60^\circ\text{C}$ , there was a moderate conversion of the feed and a relatively high selectivity to the primary liquid product. However, above  $60^\circ\text{C}$ , there was a step change in the amount of isomerization, which resulted in significantly higher conversions and significantly lower selectivities. An experiment with a temperature ramp over time located this step change in isomerization by suggesting that this temperature occurred between  $60$  and  $70^\circ\text{C}$ .

## INTRODUCTION

Olefin metathesis is an equilibrium catalyzed reaction that cleaves the double bonds in olefins and redistributes the alkene fragments into a statistical distribution of olefins. Reaction 1 represents the most generic olefin metathesis reaction.



Here, both R and R' can be alkyl groups or hydrogen. Reaction 1 is a self-metathesis, or a metathesis between two identical olefins. The alternative is a cross-metathesis, or a metathesis between two different olefins. A specific example for an olefin metathesis is shown in Figure 1.



Figure 1. Example olefin metathesis reaction: 2-octene self-metathesis.

Figure 1 shows a self-metathesis of 2-octene producing both a lighter product (2-butene) and a heavier product (6-dodecene). The first industrial metathesis reaction was the Phillips Petroleum Corporation Triolefin Process for the production of ethylene and 2-butene from propylene. More recently, olefin metathesis has been applied to three areas: synthetic organic chemistry for the synthesis of biological compounds, design of future production scale processes, and

current commercial productions of specialized olefins and polymers.<sup>1</sup> The success of an olefin metathesis process is strongly tied to the success of the catalyst system selected. Numerous catalyst systems have been developed over the last few decades, the most common involving molybdenum (Mo), tungsten (W), ruthenium (Ru), or rhenium (Re). Proper selection of a catalyst system for a specific process must be made based on catalyst activity, lifetime, durability, and regenerability. Once an appropriate catalyst is selected, the equilibrium reaction can then react medium (molecular weight) olefins into both a lighter olefin and heavier olefin, thus producing a broad range of volatilities of reactants and products.

## EXPERIMENTAL SECTION

**Bench Scale Reactor Process.** An experimental design was conducted to uncover important fundamental information for metathesis reactions based on multiple variables: weight hourly space velocity (WHSV), reactor temperature, and carbon number of the olefin feed. Figure 2 shows a process flow diagram of the bench scale reactor experiment.

This bench scale process consisted of a fixed catalyst bed for the liquid phase metathesis reaction. Nitrogen at 6.4 atm was used to pressurize the liquid feed through a liquid flow controller and then through a guard bed to remove any

**Received:** September 1, 2014

**Revised:** November 5, 2014

**Accepted:** November 13, 2014

**Published:** November 13, 2014

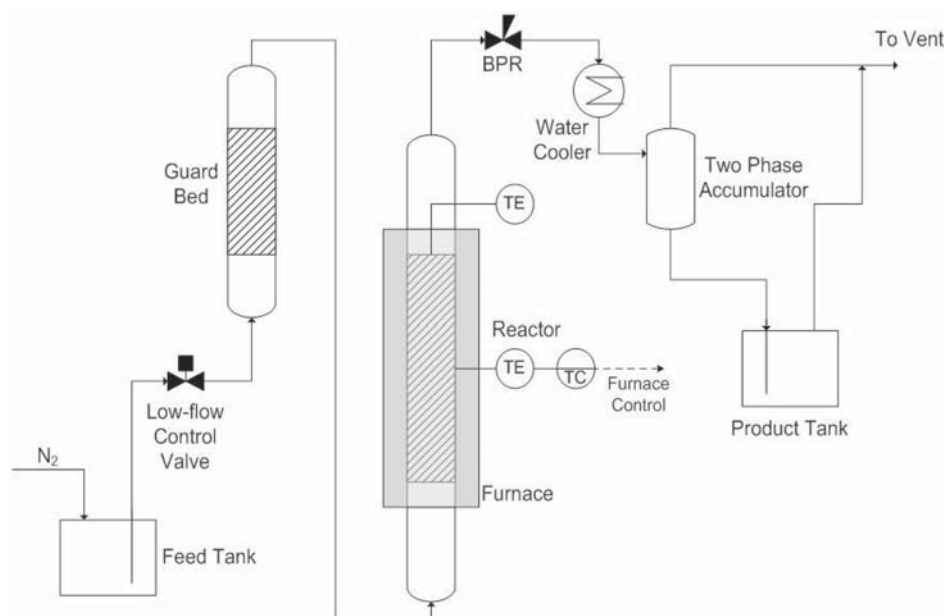


Figure 2. Bench reactor experiment process flow diagram for olefin metathesis.

impurities or contaminants. This guard bed contained Dynocel 616 1.6 mm spheres (Porocel Industries). The liquid feed was then sent to the reactor/furnace assembly. The feed line was coiled around the reactor within the furnace in order to preheat the feed prior to entering the catalyst bed. This liquid was heated while traveling down to the bottom of the reactor then fed up through the reactor. The reactor was composed of five layers of materials: glass wool at the entrance, glass beads prior to the furnace zone, catalyst, glass beads after the furnace zone, and glass wool at the exit. The glass wool was used to prevent particulates from clogging the tube entrance and exit. The glass beads were used for inert space filler and flow distribution. The catalyst was rhenium oxide (9 wt %) on  $\gamma$ -alumina. The catalyst zone contained 255 g of metathesis catalyst. The reactor was 140 cm in length and 3.8 cm in diameter. Figure 3 illustrates how the reactor was filled and the approximate dimensions.

A split-hinged round tubular furnace was used for the reactor heat source. A single zone digital controller was used to control the skin temperature of the reactor. A back pressure regulator was installed just downstream of the reactor and held a steady pressure of 2.7 atm within the reactor. The exiting product stream was collected in a vertical collection vessel to separate any vapor from the liquid products. Liquid product was accumulated in a 11 L product tank and vapor product was vented into a hood. Sampling was done on the liquid product entering the product tank. All analysis was performed using a Hewlett-Packard 5890 series GC. Third party extensive gas chromatography–mass spectrometry (GC–MS) and NMR analytical work was also used.

**Bench Scale Reactor Experimental Design.** The experimental design goal for the bench scale reactor experiments was to uncover reaction information for the self-metathesis reaction of various  $\alpha$ -olefins at a variety of conditions. Two different experiments were conducted. The first involved operating multiple feedstocks. Three  $\alpha$ -olefins were used as feeds: 1-hexene (99.56%), 1-octene (99.7%), and 1-decene (99.4%). All feed material was provided by Shell Chemical Company and each feed was given a unique

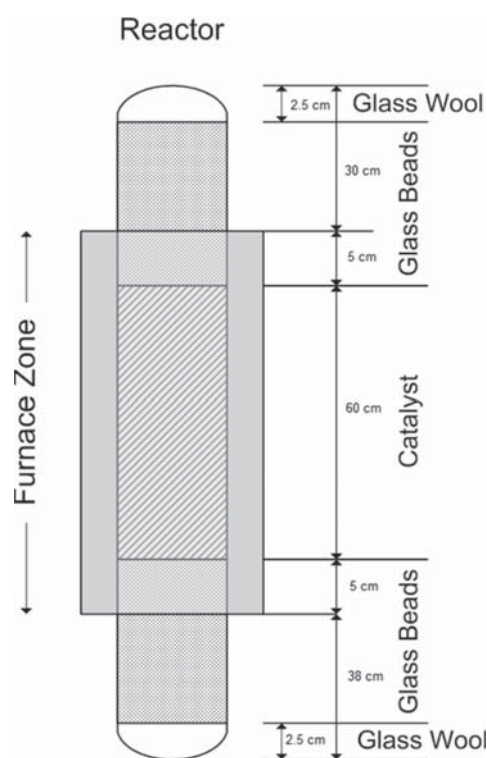


Figure 3. Bench reactor experiment detailed reactor fill schedule.

experiment number. For each feed (or experiment number), there were four runs performed: high flow with low temperature, high flow with high temperature, low flow with low temperature, and low flow with high temperature.

The low and high temperatures were the desired temperatures for the process outlet temperature measurement. These values were 70 and 93 °C, respectively. The low and high flow rates were the desired flow rates that would provide WHSV values of approximately 0.2 and 0.4 h<sup>-1</sup>. The flow rates were

Table 1. Conversions and Selectivities for the First Designed Set of Experiments

experiment	experiment 1A (1-hexene) total conversion of feed (%)	experiment 1A (1-hexene) selectivity of primary product (%)	experiment 1B (1-octene) total conversion of feed (%)	experiment 1B (1-octene) selectivity of primary product (%)	experiment 1C (1-decene) total conversion of feed (%)	experiment 1C (1-decene) selectivity of primary product (%)
run 1: 70 °C, 0.4 h <sup>-1</sup>	83.63	51.26	72.98	48.73	80.23	37.07
run 2: 93 °C, 0.4 h <sup>-1</sup>	85.53	35.89	89.23	25.32	90.98	16.79
run 3: 70 °C, 0.2 h <sup>-1</sup>	87.09	34.76	66.67	71.37	70.94	47.03
run 4: 93 °C, 0.2 h <sup>-1</sup>	82.70	44.90	92.23	13.04	90.23	12.99

50.0 g/h for a WHSV of 0.20 h<sup>-1</sup> and 100.0 g/h for a WHSV of 0.40 h<sup>-1</sup>. Experiment 1A, run 1 represented a run of 1-hexene as the feed at 100.0 g/h with an outlet process temperature of 70 °C.

The second experiment was an investigation of the impact temperature had on the frequency of side reactions. Therefore, this study was conducted over a broader span of temperatures than the first set of experiments. Two  $\alpha$ -olefins feedstocks (again provided by Shell Chemical Company) were used: 1-octene and 1-decene. For each feed, duplicate runs were conducted at a single temperature. The temperatures used were ambient (19–22), 40, 60, and 80 °C. All runs were conducted at 100.0 g/h for a WHSV of 0.4 h<sup>-1</sup>. This WHSV value was selected so that it was comparable with the first set of experiments.

Operational protocol did not vary between the two designed sets of experiments. Prior to each run, feed material filled the system through a bypass line around the flow controller until a steady liquid rate was acquired at the sample point. This confirmed that the reactor was liquid full. If the reactor was still liquid full from a previous run, then the reactor was flushed for at least 45 min with fresh feed. After either a filling of the system or flushing of the system, the experimental flow rate was set and furnace was turned on. Sampling was performed every subsequent hour and process outlet temperatures were recorded every 15 min until the desired temperature was reached. Once consecutive steady outlet concentrations were acquired, the run for the experiment was complete. Typically after four or five runs, the catalyst bed required regeneration. The reactor was purged with nitrogen the day before regeneration was necessary. To begin the regeneration, the reactor was heated up to 300 °C. Oxygen, via bottled air, was blended with the nitrogen purge and fed into the reactor with an approximate total oxygen concentration of 0.5% mol. The reactor temperature was then increased and held constant at approximately 350–360 °C. The oxygen concentration was slowly increased every hour until the total concentration was approximately 10% oxygen. Once all observed exotherms had passed through the reactor, the furnace heat was turned off and the reactor was cooled down overnight with a nitrogen purge.

## RESULTS AND DISCUSSION

**First Designed Experiment: Conversion and Selectivity Results.** The first designed set of experiments performed on the bench reactor apparatus used three different carbon number feedstocks at the four run conditions. Table 1 shows the total conversions for each run and the selectivity to the primary liquid metathesis product for each of the twelve runs performed for this designed set of experiments.

Tables 2–4 present results for experiment 1 (1-hexene, 1-octene, and 1-decene). These tables clearly show the change in product distribution throughout the duration of each run.

Table 2. Experiment 1A (1-Hexene) Reactor Product Composition (wt %)

component	run 1	run 2	run 3	run 4
C5-	4.8	10.0	4.0	9.0
C6 (reactant)	16.4	14.8	12.6	17.3
C7	9.2	10.5	7.1	9.9
C8	4.8	7.5	2.0	4.7
C9	15.6	17.1	9.6	15.2
C10 (primary product)	42.9	29.8	28.6	37.1
C11+	6.3	8.2	36.1	5.2

Table 3. Experiment 1B (1-Octene) Reactor Product Composition (wt %)

component	run 1	run 2	run 3	run 4
C7-	7.5	7.5	3.5	20.0
C8 (reactant)	27.3	11.8	30.8	7.4
C9	5.6	11.6	4.0	10.2
C10	1.0	5.2	0.7	9.4
C11	2.0	5.7	1.0	8.4
C12	3.5	10.0	1.3	9.0
C13	12.1	17.3	9.1	10.3
C14 (primary product)	37.2	23.3	48.3	11.6
C15+	3.8	7.6	1.3	13.7

Table 4. Experiment 1C (1-Decene) Reactor Product Composition (wt %)

component	run 1	run 2	run 3	run 4
C9-	5.5	12.5	6.0	14.8
C10 (reactant)	18.7	8.8	28.5	8.9
C11	10.3	11.3	10.0	11.1
C12	1.5	6.6	1.0	8.6
C13	1.3	4.8	1.0	6.4
C14	1.6	3.2	1.1	5.9
C15	3.5	6.2	2.0	6.8
C16	6.5	9.0	3.5	8.3
C17	15.6	12.6	12.0	9.7
C18 (primary product)	31.3	15.1	33.0	10.7
C19+	4.2	9.9	1.9	8.8

**First Designed Experiment: Experiment 1A (1-Hexene).** Tables 1–4 can be used to draw conclusions about the reactivity of  $\alpha$ -olefins based on changes in temperature and WHSV (or flow rate). Analysis of the experiment 1A results provided insight in the reactivity of 1-hexene with respect to temperature and WHSV. For experiment 1A (1-hexene feed), the self-metathesis of 1-hexene yielded a primary heavy liquid product of 5-decene. There was no discernible effect of temperature or WHSV on the total conversion of the feed because the conversions ranged from 82.7% to 87.09%. There were also contrasting observations for the effect that temperature and WHSV had on the selectivity of the primary liquid



Table 5. Reorganization of Conversions and Selectivities Based on Carbon Number for the First Set of Experiments

feed	run 1: 70 C, 0.4 h <sup>-1</sup> total conversion of feed (%)	run 1: 70 C, 0.4 h <sup>-1</sup> selectivity of primary product (%)	run 2: 93 C, 0.4 h <sup>-1</sup> total conversion of feed (%)	run 2: 93 C, 0.4 h <sup>-1</sup> selectivity of primary product (%)	run 3: 70 C, 0.2 h <sup>-1</sup> total conversion of feed (%)	run 3: 70 C, 0.2 h <sup>-1</sup> selectivity of primary product (%)	run 4: 93 C, 0.2 h <sup>-1</sup> total conversion of feed (%)	run 4: 93 C, 0.2 h <sup>-1</sup> selectivity of primary product (%)
1-Hexene	83.63	51.26 - C10	85.53	35.89% - C10	87.09	34.76 - C10	82.70	44.90 - C10
1-Octene	72.98	48.73 - C14	89.23	25.32 - C14	66.67	71.37 - C14	92.23	13.04 - C14
1-Decene	80.23	37.07 - C18	90.98	16.79 - C18	70.94	47.03 - C18	90.23	12.99 - C18

metathesis product. In one case, comparing run 1 to run 2, an increase in temperature decreased the selectivity. Yet in the other case, comparing run 3 to run 4, an increase in temperature increased the selectivity. With respect to WHSV, comparing run 1 to run 3, a decrease in WHSV decreased the selectivity. But, comparing run 2 to run 4, a decrease in WHSV increased the selectivity. Specifically for 1-hexene as a feedstock, it was concluded that this  $\alpha$ -olefin was highly reactive for both metathesis and isomerization in the liquid phase under the experimental conditions. For this reason, no noticeable trends in conversion and selectivity with respect to changes in temperature or WHSV were able to be deduced. Experiment 1A provided inconclusive results.

**First Designed Experiment: Experiment 1B (1-Octene).** Analysis of the experiment 1B results provided insight in the reactivity of 1-octene with respect to temperature and WHSV. For experiment 1B (1-octene feed), the self-metathesis of 1-octene yielded a primary heavy liquid product of 7-tetradecene. The total conversion of 1-octene increased with an increase in temperature under constant flow rates (run 1 to run 2 and run 3 to run 4). Furthermore, an increase in temperature also resulted in a drastic decrease in selectivity to the primary product. Based on the observation that isomerization was more common at higher temperatures, increased isomerization of the feed would result in both an increase in conversion and a decrease in selectivity primary product. More of the feed was isomerized and these isomerized molecules would then follow-up with subsequent metathesis, forming secondary products. With respect to WHSV, under a constant low temperature setting, a reduction in WHSV resulted in a slight decrease in conversion, but a dramatic increase in selectivity. A reduction in flow would have decreased mass transfer to the catalyst active site through the pores. A reduced diffusion through the catalyst pores would then have decreased the production of any product that needed the active site at the base of the pore. This would have resulted in a drop in total conversion of feed. However, this did not justify the increase in selectivity. It was possible that for 1-octene, a low flow rate and low temperature was the most optimal operating condition that would maximize self-metathesis of 1-octene and minimize secondary isomerization and subsequent metathesis for this bench reactor apparatus. Under a constant high temperature setting, a reduction in WHSV resulted in no real change in total conversion and a decrease in selectivity. A high temperature likely promoted high activity of both metathesis and isomerization regardless of flow rate, suggesting that a reduction in mass transfer through the catalyst pores did not affect the total conversion of the feed. This observation could have been explained by a possible source of the isomerization. If the isomerization was occurring on the surface of the catalyst support (or catalyzed by the alumina), then a reduction in diffusion through the catalyst pores would not have decreased the isomerization activity. Furthermore, less diffusion and

metathesis at the catalyst active site would have also decreased the selectivity of the primary product.

**First Designed Experiment: Experiment 1C (1-Decene).** Analysis of the experiment 1C results provided insight in the reactivity of 1-decene with respect to temperature and WHSV. For experiment 1C (1-decene feed), the self-metathesis of 1-decene yielded a primary heavy liquid product of 9-octadecene. Similar to experiment 1B, the total conversion of 1-decene increased with an increase in temperature under constant flow rates (run 1 to run 2 and run 3 to run 4). Also similar to experiment 1B was the decrease in selectivity with an increase in temperature. Higher temperatures promoted higher isomerization, and therefore increased total conversion of the feed and increased selectivity of secondary products. With respect to WHSV, similar observations to experiment 1B were made. Under a constant low temperature setting, a decrease in WHSV resulted in a decrease in conversion, but an increase in selectivity to the primary product. For the same reasons outlined before, it was similarly concluded that a low flow and low temperature condition could have been the most optimal condition for maximizing the self-metathesis of 1-decene and minimizing secondary isomerization and subsequent metathesis. Under a constant high temperature setting, a decrease in WHSV resulted in no change in conversion and a slight decrease in selectivity. For the same reasons outlined before, if the secondary isomerization was occurring on the surface of the catalyst support, then there would be an observed decrease in selectivity with decreased flow rate and diffusion, but no real change in total conversion of the feed.

**First Designed Experiment: Effect of Carbon Number of Reactivity.** The conversion and selectivity data for each experiment was previously used to compare performances between run conditions and to get an understanding on the effect reactor temperature and flow rate (WHSV) had on the reaction performance. But Table 1 can be reorganized to illustrate the impact carbon number had on the conversion and selectivity. Table 5 presents this reorganization.

Looking at Table 5, some general observations about the effect of carbon number on the reaction performance could be made. Under a high temperature condition (both run 2 and run 4), all three feedstocks showed very high activity with a gradual increases in conversion with increasing chain length, but a significant decrease in selectivity to primary product with increasing chain length. As the chain length increased, the larger the number of different possible isomers there could have been. For an isomerization of 1-hexene, there were only three skeletal isomers that could have existed. But for an isomerization of 1-decene, there were five skeletal isomers that could have existed. Isomerization of longer chain length olefins resulted in more possibilities of reactant pairs for a metathesis reaction. Higher possibilities meant more possible products that were not the primary heavy liquid product. In essence, when temperature and isomerization were high, the longer chain olefin was more reactive than the shorter chain olefin for both metathesis and

isomerization. This observation was independent of flow rate. Under a low temperature condition (both run 1 and run 3), the highest selectivities of all twelve runs were observed. This indicated that temperature definitely had a strong impact on the performance of this reaction network. The lower the temperature, the narrower the product distribution. However, also under a constant low temperature, there was no distinguishable relationship for carbon number in the feed with respect to flow rate. It was concluded that with this designed set of experiments, no quantitative assessment could be made about the reactivity of  $\alpha$ -olefins with respect to carbon number.

**Second Designed Experiment: Conversion and Selectivity Results.** The second designed set of experiments performed on the bench reactor apparatus utilizing 1-octene and 1-decene feedstocks at a broad range of temperatures. Table 6 (1-octene) and Table 7 (1-decene) show the total

**Table 6. Conversions and Selectivities for Second Designed Set of Experiments of Bench Reactor Experimentation with 1-Octene**

temperature	run title	total conversion of feed (%)	selectivity of primary product C14 (%)
ambient	run 1	36.31	81.22
	run 2	27.07	91.17
40 °C	run 1	49.48	88.80
	run 2	43.71	91.10
60 °C	run 1	52.98	88.84
	run 2	46.49	90.00
80 °C	run 1	88.94	28.69
	run 2	77.70	50.69

conversion and the selectivity to the primary liquid metathesis product of each run performed for this designed set of experiments.

**Table 7. Conversions and Selectivities for Second Designed Set of Experiments of Bench Reactor Experimentation with 1-Decene**

temperature	run title	total conversion of feed (%)	selectivity of primary product C18 (%)
ambient	run 1	26.64	80.97
	run 2	25.85	82.63
40 °C	run 1	55.64	77.66
	run 2	62.25	81.20

For each temperature condition, two runs were performed. Tables 8 and Table 9 present the experimental results based on end of run conditions for each experiment.

**Second Designed Experiment: Observations and Analysis.** Upon review of Tables 8 and 9, some general observations about this second designed set of experiments

**Table 9. Experiment 2B Reactor Product Composition (wt %) WHSV = 0.4/h**

component	run 1A (ambient)	run 1B (ambient)	run 2A (T = 40 °C)	run 2B (T = 40 °C)
C9-	2.5	2.0	2.5	2.0
C10 (reactant)	70.5	75.8	45.5	36.2
C11–C17	3.2	2.2	10.3	10.3
C18 (primary)	23.8	20.0	41.7	51.5
C19+				

were made. Of the twelve runs performed, ten of them had very high selectivities coordinating with moderate total conversions of the feed. For these ten runs, the total conversions ranged from 25.85% to 62.25% and the selectivities ranged from 77.66% to 91.17%. All ten of these runs were performed at ambient conditions, 40 or 60 °C. Duplicate runs produced a slight variation in the conversion and selectivity values of approximately 3% to 5% on a mass basis. This variation could be attributed to the fact that the catalyst was losing activity; in every instance, the total conversion was lower in run 2 than in run 1. The two outlying runs were the two performed at 80 °C for 1-octene; each had very high conversion with relatively low selectivity. The total conversion was approximately 83.32% and the selectivity was approximately 38.95%.

The products from both a 40 and 60 °C run of the 1-octene runs were analyzed for the degree of branching using GC and NMR. It was confirmed that for both of these temperatures, the total degree of branching was less than 0.5%. For branching that did occur, it was confirmed to only be branching of the olefinic carbon atoms and not the aliphatic carbon atoms.

It was clear that temperature played a strong role in the occurrence of isomerization. Up until 80 °C, there was minimal isomerization as all of the other ten runs had very high selectivities. By increasing the temperature from ambient conditions to 60 °C, the total conversion gradually increased with the selectivity maintaining a relative steady high value. From the first designed set of experiments, the lower temperature runs for 1-octene were performed at 71 °C and were used to support this trend. These two runs at 71 °C both had approximately 69% conversion and 60% selectivity; these values fit into this observed trend. However, for the second set of designed experiment runs, there was also a significant step change in the amount of isomerization between 60 and 80 °C. It was possible that the activation energy necessary for the isomerization of these  $\alpha$ -olefins was attained from some temperature between 60 and 80 °C.

Between 1-octene and 1-decene, there was no trend with respect to reactivity based on carbon number. Under ambient conditions, 1-octene had a higher conversion and a higher selectivity. But at 40 °C, 1-decene had a higher conversion and a lower selectivity. For this reason, no quantitative assessment

**Table 8. Experiment 2A Reactor Product Composition (wt %) WHSV = 0.4/h**

component	run 1A (ambient)	run 1B (ambient)	run 2A (T = 40 °C)	run 2B (T = 40 °C)	run 3A (T = 60 °C)	run 3B (T = 60 °C)	run 4A (T = 80 °C)	run 4B (T = 80 °C)
C7-	1.2	0.8	0.7	1.2	1.5	1.5	9.0	6.5
C8 (reactant)	65.2	72.8	51.0	55.3	47.0	52.9	11.2	22.0
C9–C13	3.8	1.4	4.8	3.4	4.6	3.1	46.5	28.8
C14 (primary)	29.8	25.0	43.5	40.1	46.9	42.5	25.3	38.7
C15+							8.0	4.0

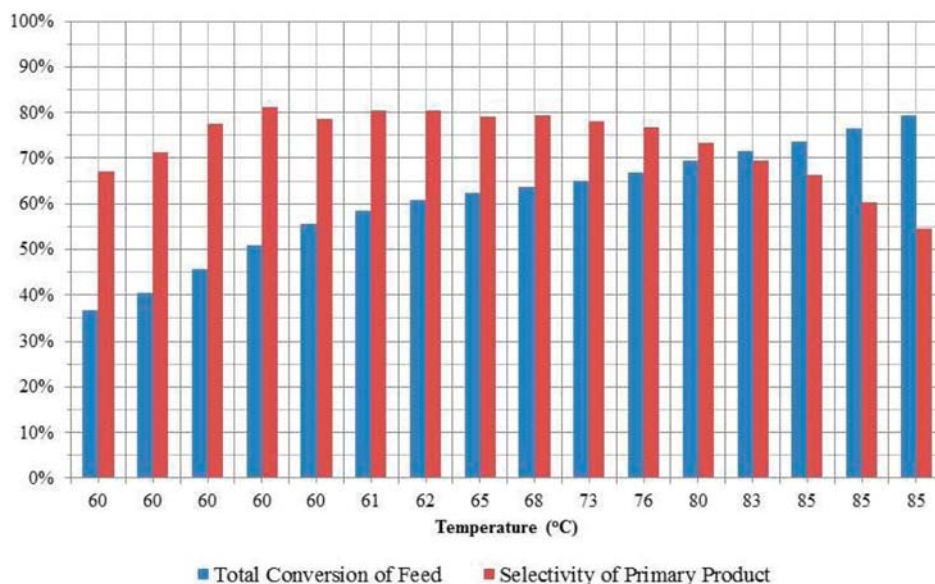


Figure 4. Conversions and selectivities for temperature ramp run.

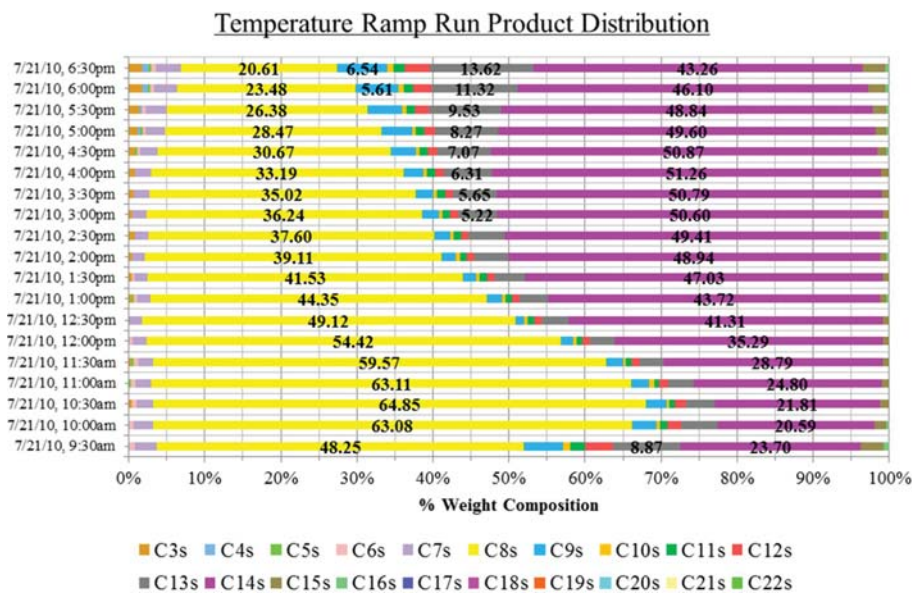


Figure 5. Bench reactor product weight composition versus time for temperature ramp run.

could have been made about the reactivity of  $\alpha$ -olefins with respect to carbon number.

**Second Designed Experiment: Temperature Ramping.** In the previous section, it was concluded that there existed a temperature between 60 and 80 °C that resulted in a significant step change in isomerization and therefore an observable change in total conversion and selectivity. In order to investigate this range further, another run was performed with a temperature ramping providing a constant change in reactor temperature. The reactor was raised to 60 °C, held constant for 2 h, and then steadily increased by 2 °C every 20 min to 85 °C. Figure 4 and Figure 5 show the change in product distribution throughout the duration of this temperature ramp run.

As Figure 4 illustrates, when temperature was steadily increased, conversion also steadily increased. Notable was the

steady increase in conversion while the reactor temperature was held constant at 60 °C. This increase in conversion represented the continued progression of the liquid products exiting the catalyst bed, but still having to pass through the inert glass bead section to reach the sample point. As Figure 4 illustrates, there was also a definite point between 60 and 80 °C where the selectivity was maximized. Identification of the exact temperature where this maximum selectivity occurred was difficult because the selectivity maintained an approximate value of 80% for almost 2 h. Furthermore, the sample taken at each time was actually representative of the product exiting the reactor at least an hour earlier due to the residence time required to pass through the inert glass beads and condenser prior to the sample point. Therefore, there was a lag time between what the current sample represented and the temperature that was recorded at least an hour earlier. Analysis of the second designed set of



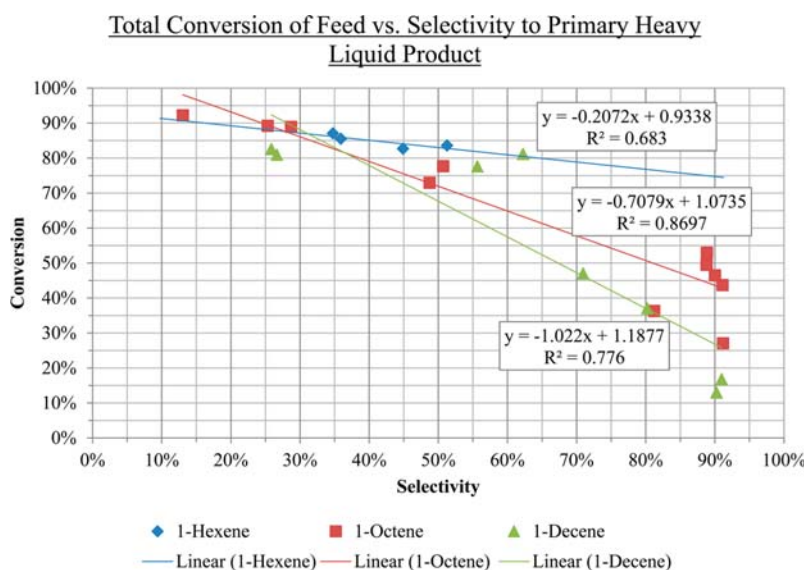


Figure 6. All bench reactor data plotted as conversion versus selectivity.

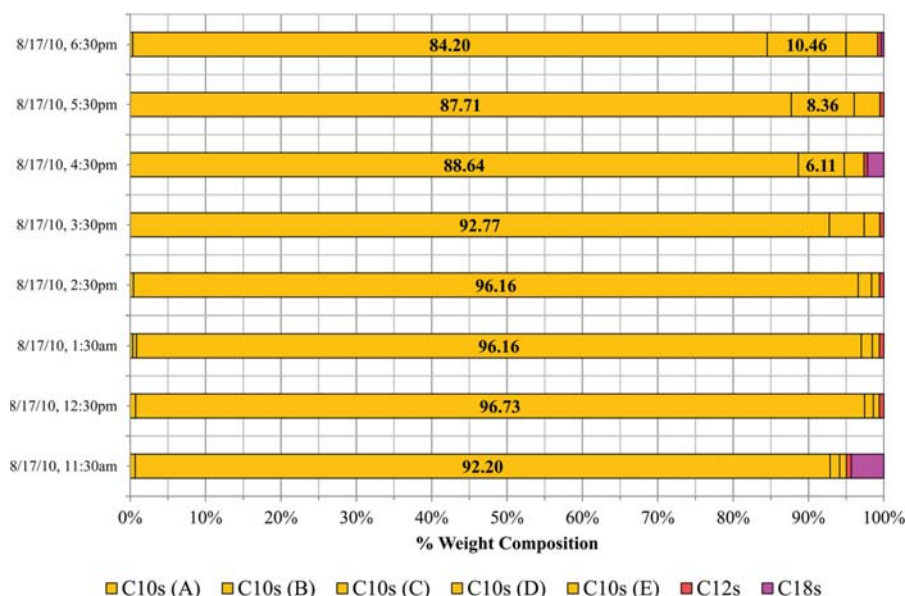


Figure 7. Bench reactor product weight composition versus time for inert alumina supports for 200 °F and a WHSV of 0.2 h<sup>-1</sup>.

temperatures concluded that there was a noteworthy point between 60 and 80 °C. Analysis of this temperature ramping run concluded that this range was more likely between 60 and 70 °C. A more refined version of this temperature ramping schedule would possibly be able to help identify this unknown transition temperature.

## BENCH REACTOR EXPERIMENTATION: OVERALL DATA COMPARISON

It was beneficial to look at all of the bench reactor experimental data from both designed sets of experiments together in hopes of discerning some overall trend. Figure 6 shows all of the data plotted together in the form of total conversion of the feed versus selectivity of the primary product for all three of the  $\alpha$ -olefins investigated. Figure 6 also includes linear trend lines for each of the different  $\alpha$ -olefins.

Disregarding carbon number, there was clearly a trade-off between conversion and selectivity. High conversion, as a result of higher temperatures and therefore higher isomerization, was coupled with low selectivity due to secondary isomerization and metathesis reactions. High selectivity, as a result of lower temperatures and therefore lower isomerization, was coupled with low conversion because these metathesis reactions have all been shown to have a moderate dependence on temperature. With respect to carbon number, there appeared to be an observable effect selectivity had on conversion. The data suggests that the heavier the olefin, the stronger the effect selectivity had on conversion. Therefore, a self-metathesis of 1-decene would have showed a more drastic change in conversion with smaller changes in selectivity.

**Metathesis Catalyzed Isomerization: Possible Sources and Explanation.** The initial intent of the both of the designed sets of experiments was to uncover information on the

olefin metathesis reactions under very controlled experimental conditions. However, as the most previous results have shown, there was a very high degree of isomerization present in some of the runs. Trying to interpret conversion and selectivity of a metathesis reaction when other side isomerization reactions were occurring made it nearly impossible to ascertain detailed kinetic information on specific metathesis reactions. The source of this isomerization could have been one of many things, and it was important to determine what may have caused this undesired secondary isomerization in hopes of avoiding it in future experimentation.

It has been suggested that, due to possible impurities, alumina can be an active double-bond isomerization catalyst.<sup>2</sup> Impurities such as silicon can create isomerization activity even with concentrations in the ppm level. Therefore, it was possible that the actual catalyst support ( $\gamma$ -alumina) was a source of this isomerization. To determine if this was indeed the isomerization cause, a series of experiments with inert alumina supports was conducted. The support material was regenerated and then tested for isomerization activity by performing tests at two conditions: a flow rate of 50 g/h (WHSV = 0.39 h<sup>-1</sup>) and 93 °C representing the highest anticipated isomerization and a flow rate of 100 g/h (WHSV = 0.20 h<sup>-1</sup>) and 40 °C representing the lowest anticipated isomerization. Figure 7 shows a similar stacking bar graph for this first condition, but this stacking bar graph has a few modifications.

For simplicity, only carbon numbers detected in the product were included. As can be seen in Figure 7, there were five different decene isomers detected. All of the decene bars have been colored the same, but outlined to highlight the changes in concentration between each isomer. As can be seen, at the highest assumed isomerization condition, approximately 15% of the 1-decene feed was being isomerized. The lowest assumed isomerization condition showed no difference in concentration profile between isomers when compared to the composition of the feed upstream of the reactor. It was likely that the elevated temperature, and not the reduced flow rate, played a stronger role in creating isomerization. Nevertheless, it has been shown here that the same inert alumina supports used as the metathesis catalyst substrate were a possible source of the observed isomerization present among the sets of designed experiments previously performed.

Another possible source of isomerization was that dehydrogenation of olefins could have been occurring. The rhenium oxide active site could have caused a pair of hydrogen atoms away from the double bond to be removed and exit the reactor as hydrogen gas. This would have created a diolefin, and there would then be two double bond locations for metathesis to occur. Past studies have suggested that internal olefins were more reactive than terminal olefins.<sup>3</sup> Diolefins are not the same as internal olefins; however, it was possible that the more internal double bond of a diolefin was more reactive for metathesis than the more terminal double bond. A good test to determine whether dehydrogenation was occurring would be to take a gas sample on the vapor outlet and measure for hydrogen. If no hydrogen was present, then dehydrogenation could not have occurred.

There was another possible test that could be used to further understand this undesirable isomerization. If the reactor was fed with a symmetric olefin (2-butene, 3-hexene, or 4-octene), then metathesis could not occur without isomerization. A symmetric isomer in a trans orientation should be the most thermodynamically stable position for a linear olefin; therefore,

isomerization should really not occur. But if any other compound were to exit with the reactor effluent, then that would mean isomerization followed by metathesis would have had to occur.

## CONCLUSIONS

A variety of specialized bench reactor experiments were performed to yield valuable kinetic information for specific metathesis reactions. The underlying conclusion from these bench reactor experiments was that under the necessary pilot plant conditions, there was a high degree of isomerization occurring over this metathesis catalyst. For this reason, only general qualitative assessments could be made about the reactivity of olefins with respect to temperature, flow rate, and carbon number in the feed.

The first set of experiments was designed to observe the impact temperature and WHSV had on the reactivity of three different  $\alpha$ -olefins. The investigated temperatures and WHSV were conditions that encompassed the anticipated reactive distillation column reactor zones temperatures and WHSV. All of these runs displayed high conversions, low selectivities, and significant secondary isomerization coupled with subsequent metathesis. This isomerization compromised the ability to make any quantitative assessments on the reactivity of olefins with respect to temperature, flow rate, and carbon number in the feed. However, it was concluded that there was a possible optimal condition of a low flow and low temperature. This prompted further bench reactor experimentation.

The second set of experiments was designed to observe the impact temperature had on conversion and selectivity of two different  $\alpha$ -olefins. These experiments concluded that between an ambient temperature condition and 60 °C, there was a moderate conversion of the feed and a relatively high selectivity to the primary liquid product. However, above 60 °C there was a step change in the amount of isomerization, which resulted in significantly higher conversions and significantly lower selectivities. An experiment with a temperature ramp over time helped locate this step change in isomerization by suggesting that this temperature occurred somewhere between 60 and 70 °C.

An overall qualitative assessment of the bench reactor experiments suggested a trade-off between conversion and selectivity. High conversion only occurred with low selectivity and high selectivity only occurred with low conversion. However, the undesired isomerization prevented any quantitative analysis of the reactivity of heavy olefins from being done. An experimental test of the reactivity of inert alumina supports for isomerization was performed and it was concluded that the  $\gamma$ -alumina utilized for metathesis was indeed active for isomerization under high temperatures. Future experiments designed to help ascertain the source of this isomerization would help uncover more kinetic information about this specific system being investigated.

## AUTHOR INFORMATION

### Corresponding Author

\*R. B. Eldridge. E-mail: eldridge@che.utexas.edu.

### Notes

The authors declare no competing financial interest.



## ■ REFERENCES

- (1) Ivin, K.; Mol, J. *Olefin Metathesis and Metathesis Polymerization*; Academic Press, San Diego, CA, 1997.
- (2) Kapteijn, F.; Mol, J. Stereochemistry in Metathesis of n-Alkenes Using Heterogeneous Oxide Catalysts. *J. Am. Chem. Soc.* **1982**, *78*, 2583–2592.
- (3) Kawai, T.; Goto, H.; Yamazaki, Y.; Ishikawa, T. Metathesis of n-Alkenes over a CsNO<sub>3</sub>-Re<sub>2</sub>O<sub>7</sub>-Al<sub>2</sub>O<sub>3</sub> Catalyst. *J. Mol. Catal.* **1988**, *46*, 157–172.