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Sustainable Solid Catalyst Alkylation of Commercial Olefins by Regeneration with Supercritical Isobutane

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Supercritical isobutane regeneration of an ultrastable Y-zeolite (USY) alkylation catalyst was examined in a continuous, automated reaction/regeneration system. Two feeds were studied: a synthetic isobutane/2-butene blend and a commercial refinery isoparaffin/olefin blend. Synthetic feed experiments showed that high levels of butene conversion were maintained for a time on stream of more than 200 h, and that product quality and catalyst maintenance was relatively stable over the course of the experiment, using a 3 h reaction/3 h regeneration cycle. Thirty five reaction/regeneration cycles were conducted over 210 h using the synthetic feed. Over this period, butene conversion did not drop below 92% until the end of the experiment. The average butene conversion declined 0.051% per run, and the average C_8 and trimethylpentane (TMP) composition decreased only 0.082% and 0.06%, respectively, per run. Catalyst activity maintenance was lower when the commercial feed was used. High levels of alkene conversion were maintained for 78 and 192 h, using a 3 h reaction/3 h regeneration cycle and a 2 h reaction/2 h regeneration cycle, respectively. Using a 3 h reaction/3 h regeneration cycle, alkene conversion remained at or above 92% for 13 reaction/regeneration cycles, corresponding to 78 h of semicontinuous operation. Using a 2 h reaction/2 h regeneration cycle, the alkene conversion did not drop below 92% until the end of 48 reaction/regeneration cycles, corresponding to 192 h of operation. The 2 h reaction/2 h regeneration cycle limited the decline in alkene conversion to 0.035% per run and limited the decline in C_8 and TMP composition to 0.040% and 0.042%, respectively, per run.

1. Introduction

Isoparaffin alkylation is utilized in the petroleum refining industry to produce a low-vapor-pressure, high-octane gasoline blend stock through the reaction of high-vapor-pressure iso-alkanes and alkenes. Alkylate is highly desired, because of its advantageous octane rating and blending properties and because it presents environmental advantages, including low sulfur, benzene, aromatics, and alkene contents. The production of alkylate is necessary to meet U.S. energy demands, because it is considered to be an essential requirement for meeting the growing need for reformulated gasoline.[1]

Current industrial alkylation processes use concentrated mineral acids, including hydrofluoric (HF) or sulfuric acid (H_2SO_4) to catalyze the reaction.[2] The processes present serious safety and environmental risks that result from the transport and storage of the concentrated liquid acids and from the need to dispose of acid−oil sludges produced as byproducts of the processes. Thus, a safe, environmentally acceptable alternative to liquid acids is highly desired. Solid acid catalysts could be used to replace these liquid acids in alkylation and thereby reduce the environmental impact of alkylation processes; however, there are significant technical hurdles to overcome before this can be implemented.

While significant advancements have been made in recent years in the development of solid acid catalysts capable of catalyzing the alkylation reaction,[3] the economics of utilizing these catalysts in the commercial production of alkylate have been poor, primarily because of rapid deactivation from the buildup of coke, difficult catalyst regeneration, poor product quality, and energy-intensive product recovery. The challenges surrounding the use of solid catalyst alkylation have been

reviewed.[3−5] A significant limitation to the use of the solid catalysts is deactivation due to the deposition and buildup of heavy hydrocarbons on the catalyst surface, forming carbonaceous deposits that cover active catalyst sites and plug the catalyst pore structure, resulting in significant catalyst deactivation in short periods.[3,6] Traditional methods of regenerating solid catalysts, such as oxidation and hydrogenation, while generally effective at removing the deposits, are often incomplete,[7] damage the catalyst,[8] or require the presence of noble metals in the catalyst and an extensive hydrogen supply infrastructure. These factors all serve to increase capital and operating costs significantly.

An alternate method that has shown promise for regenerating solid catalysts deactivated by carbonaceous deposits is supercritical fluid (SCF) extraction.[9] The unique solvent and transport properties of SCFs, including solvent strength similar to liquids and transport properties similar to gases,[10] make SCFs highly efficient for the extraction of fouling materials from porous heterogeneous catalysts.[11] We recently reported that SCFs could be used as an off-line in situ method to regenerate a solid catalyst used in isobutane/butene alkylation.[12−17] Initially, we reported that a fully deactivated alkylation catalyst could be partially regenerated while a partially deactivated catalyst could be fully regenerated with SCFs.[12] The choice of SCF[13] and the effect of process conditions[14] on regeneration effectiveness for a completely deactivated catalyst have been reported. The effect of time on stream (TOS)[15] and zeolite pore structure[16] on the nature of the carbonaceous species deposited on the catalysts before and after SCF regeneration were also reported. More recently, we reported on the regeneration effectiveness for a partially deactivated catalyst using supercritical isobutane in a semicontinuous regeneration system.[17]

The purpose of the present study was to explore the effectiveness of supercritical isobutane for multiple regenerations of a solid acid catalyst used in isoparaffin alkylation with a

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Table 1. Compositions of the Reactor Feed Streams Used in the Alkylation/Regeneration Tests

feed component	Feed Composition	
	premixed synthetic feed[a]	commercial feed blend[b]
Alkylation Reactants (Percentage of Feed, wt %)		
isoparaffins		
isobutane	95.0 ± 0.1	91.34
isopentane	0	0.239
olefins		
C_3 olefins	0	1.215
C_4 olefins		
isobutene	0	0.833
1-butene	0	0.624
trans-2-butene	2.23 ± 0.04	0.808
cis-2-butene	2.41 ± 0.04	0.609
C_5 olefins	0	0.147
isoparaffin:olefin	20.5 ± 0.4	21.57
isobutane:olefin	20.5 ± 0.4	21.62
Impurities (ppm)		
ethane	0	19
propane	571 ± 2	8770
n-butane	3030 ± 165	32600
n-pentane	0	53
butadiene	0	122
acetone	0	9
total sulfur	0	1
unknowns	0	412

[a] Measured composition of premixed synthetic alkylation feed supplied by Matheson Tri Gas (Montgomeryville, PA). [b] Premixed commercial alkylation feed blend, as supplied by the Phillips Petroleum Company (Bartlesville, OK).

commercial alkylation feed blend. This effort was constrained to that purpose, and catalysts, reaction conditions, and regeneration conditions were not investigated here. In this paper, we present a detailed examination of supercritical isobutane regeneration of a USY zeolite alkylation catalyst in a continuous, automated reaction/regeneration system. Two feeds were studied: a synthetic isobutane/2-butene blend and a commercial refinery isoparaffin/olefin blend. The refinery blend was minimally treated, containing a variety of light olefins and contaminants, including butadiene, oxygenates and sulfur, which are well-known to cause severe catalyst deactivation. The low-quality commercial alkylation feed stream was considered a challenge case for the supercritical regeneration process.

2. Methods

2.1. Catalysts and Chemicals. A commercially available ultrastable Y-zeolite catalyst (USY, Zeolyst International, Valley Forge, PA) was used for the alkylation/regeneration experiments. This catalyst, which was used as 1.6 mm extrudates, was comprised of 59.7 wt % SiO_2, 39.5 wt % Al_2O_3, and 0.08 wt % sodium, and had a surface area of 704 m²/g, a pore volume of 0.44 cm³/g, an average pore diameter of 14 Å, and a total acidity of 1240 μmol/g. The catalyst was calcined at 400 °C for 3 h before use, as suggested by the supplier. In addition, the catalyst was dried overnight in the alkylation reactor immediately before use with flowing helium (Ultrahigh Purity, U.S. Welding, Denver, CO) at 200 °C to remove adsorbed water. Failure to perform the catalyst drying step resulted in significantly reduced catalyst performance.

Two alkylation reactant feed blends were used; their compositions are shown in Table 1. The first, a pre-blended synthetic alkylation feed, was custom-prepared by Matheson Tri Gas (Montgomeryville, PA). This feed consisted primarily of isobutane (95.0 wt %), *trans*-2-butene (2.23 wt %), and *cis*-2-

butene (2.41 wt %), with an isoparaffin:olefin ratio of 20.5 ± 0.4. The synthetic feed also contained small amounts of contaminating propane (570 ppm) and *n*-butane (3000 ppm).

The second alkylation feed, a commercial alkylation feed blend, was provided by the Phillips Petroleum Company (Bartlesville, OK). The commercial feed blend was a mix of isoparaffins and olefins from a refinery alkylation feedstream. The olefin stream was only minimally treated at the refinery with a caustic wash to remove mercaptans. The parent olefin stream contained contaminants that included butadiene (2000 ppm), acetone (140 ppm), and sulfur (16 ppm), which were considered to be detrimental to catalyst stability and, hence, a challenge for the regeneration process. The isoalkanes in the commercial blend consisted primarily of isobutane (91.3 wt %) and also a small amount of isopentane (0.24 wt %). The C_4 olefins (2.87 wt %) included 1-butene, isobutene, and *cis*- and *trans*-2-butenes. Additional olefins in the commercial feed included propylene (1.22 wt %) and several C_5 olefins (0.147 wt %). The isoparaffin:olefin ratio of the commercial feed was 21.6. The commercial feed also contained contaminating normal paraffins, including significant amounts of *n*-butane (3.26 wt %) and propane (0.877 wt %), and smaller amounts of ethane and *n*-pentane.

2.2. Automated Supercritical Fluid Reactor System. The automated SCF reactor system used in the experiments described in this article was set up to operate unattended, under the control of a Camile 2000 data acquisition and control system (Camile Products, LLC, Indianapolis, IN). Process variables were monitored by data logging, using a desktop personal computer. Reactant feed and regenerant feed were added using high-pressure syringe pumps, set to autofill when empty. The pumps were not controlled by Camille.

A schematic of the reactor/regeneration and control systems is shown in Figure 1. The system used two reactors, containing 1−10 g of catalyst (each), arranged in separate loops in a swing column configuration. Reactors were constructed from high-pressure stainless steel tubing (12.7 mm outer diameter (od) × 8.5 mm inner diameter (id)). A plug of glass wool at each end of the catalyst bed kept the catalyst in place. When reaction was occurring in reactor 1 (RXT1), regeneration was simultaneously occurring in reactor 2 (RXT2), and vice versa. Flow switching between the two columns was achieved using two six-port automated two-position high-pressure switching valves (ASV1 and ASV2). Reactants, consisting of the preblended isoalkane and olefin alkylation reactants (Rxn Mix), entered the system via feed pumps, while isobutane for the regeneration phase entered via a second pump system. Helium (>99.9% pure) was used to pressure check the system, purge the system, and dry the catalysts in the reactor before use.

The system was fed by dual 266-mL high-pressure syringe pumps (Model 260D, ISCO, Lincoln, NE) with preblended isoalkane and olefin reactants; the pumps refilled automatically when empty. At the exit of the feed pump, there was a normally closed, high-pressure solenoid valve controlled by the interlocks of the fume hood in which the system was located, as well as by the data acquisition and control system, and it was used to shut down the system under off-normal conditions. Isobutane for the regeneration was fed by dual ISCO 260 D syringe pumps in an analogous manner. Another normally closed, high-pressure solenoid valve was placed at the exit of the dual syringe pumps. There were two high-pressure pressure transducers (PTs): one just downstream of the recycle pump, and one just before the shut-off valve near the exit from the system. The system was protected with a pressure relief valve (RV) located with the first
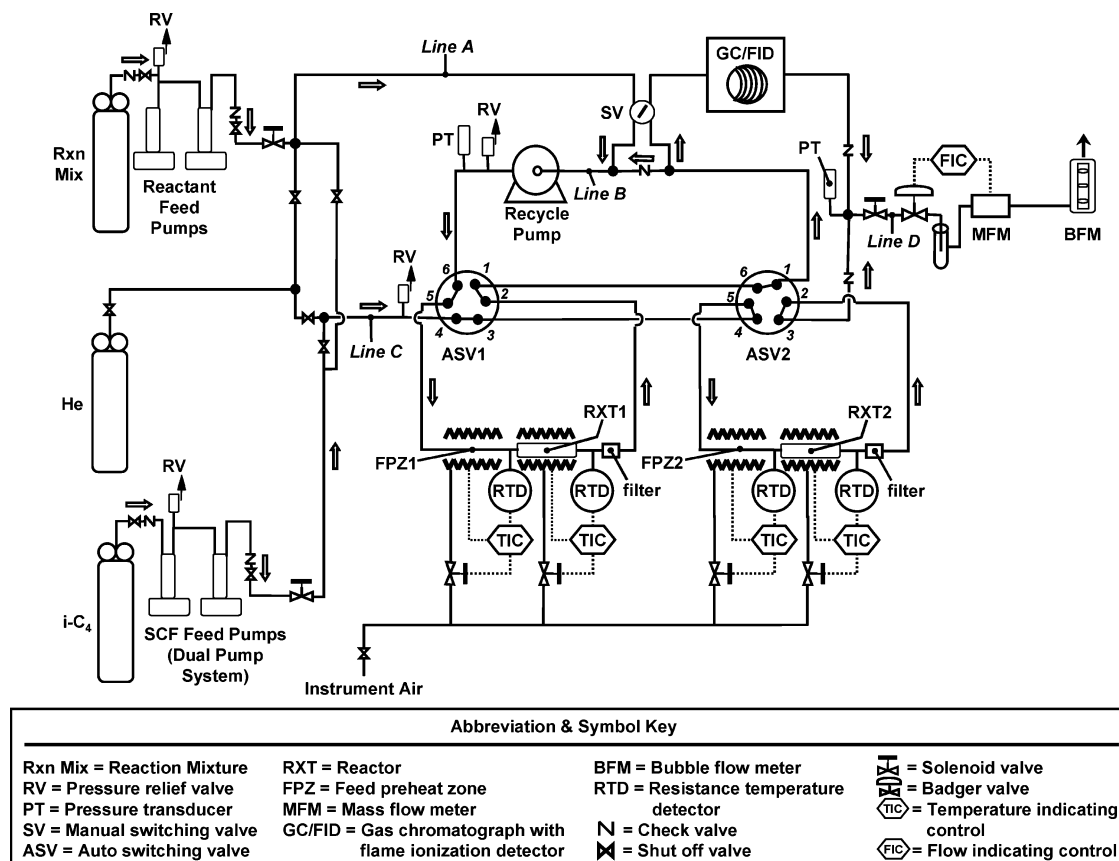
Figure 1. Schematic of the reactor and control systems. The switching valves ASV1 and ASV2 are shown such that RXT1 is the alkylating reactor and RXT2 is the regenerating reactor.

of the pressure transducers, and another RV on the recycle loop near the inlet of isobutane into the system.

Check valves (CVs) were utilized in several locations throughout the system, to guard against back flow, including between all feed pumps and their fill cylinders, between pump and cylinder inlets to the system, between inlet and outlet of the manual switching valve (SV) in the reactor loop, and at each inlet to the exit tee from the two loops (reaction and regeneration).

Both reactors were provided with separately heated preheat zones (FPZs) and reaction/regeneration zones (RXTs) using electric heaters. Each separate zone was monitored using a resistance temperature detector (RTD). Cooling was provided via house air and was controlled by the Camille system, using low-pressure solenoid valves.

2.3. Description of Operation. The system was initially filled with isobutane at 111 bar (1600 psig) in both the reaction loop (line A) and the regeneration line (line C). When the system pressure was stable at 111 bar (1600 psig), isobutane flow was set at 2 cm³/min, and the system flow, pressure, and temperature were allowed to stabilize.

A reactant feed flow (at 111 bar) was initiated at a rate of 0.25 cm³/min, traveled through line A, and mixed with the reaction recycle stream (line B). The feed entered the recycle pump operating at 45−60 cm³/min and flowed past the RV and PT. The stream then entered ASVl (in position 1) and continued to the preheat zone (FPZ1) for RXT1. The stream flowed through the catalyst bed in RXT1 and re-entered ASV1. Both FPZ1 and RXT1 were maintained at 60 °C by the Camile control system. The stream then entered ASV2 (in position 2), completing the loop by re-entering the recycle pump at line B. A bleed stream exited the reaction loop and traveled to the gas

chromatograph for analysis. Gas chromatography (GC) samples of the system effluent were acquired on-line at reaction pressure using a high-pressure sample valve with a 0.1 μL internal sample loop. The stream then continued on to the exit line tee.

Regenerant (isobutane) flow at 111 bar, 2.0 cm³/min, entered the regeneration loop (line C), flowed by the RV, and entered ASV1 (in position 1). The stream continued and entered ASV2 (in position 2) and continued to the preheat zone (FPZ2) for RXT2. The stream flowed through the catalyst bed in RXT2 to regenerate the catalyst and returned to ASV2. Both FPZ2 and RXT2 were maintained at the control temperature by the Camile control system. The stream then traveled to the exit line tee.

The reactant stream and regenerant stream were mixed at the exit line tee and entered line D, the system outlet line. The stream passed through a motor-controlled micrometering valve (controlled by Camille, using a mass flow meter (MFM)) and exited the system into the fume hood through a bubble flow meter.

At the end of the reaction/regeneration cycle, the auto switching valve positions (ASV1 and ASV2) were reversed such that reactor 1 (RXT1) was placed in the regeneration flow stream and reactor 2 (RXT2) was placed in the reaction recycle flow stream. The valves continued to switch, simultaneously, at the end of each cycle until the conclusion of the experiment.

2.4. Analytical Methods. GC analyses of the reactor effluent were performed on-line using a Hewlett−Packard 5890 Series II gas chromatograph (Wilmington, DE) that was equipped with an automated high-pressure sample valve, electronic pressure controller, flame ionization detector (FID), and thermal conductivity detector (TCD). Product separation of on-line 0.1 μL samples was achieved using a 50 m × 0.2 mm (length l × id)

Table 2. Reaction and Regeneration Conditions for the Alkylation Reaction/Supercritical Isobutane Regeneration Experiments

| feed blend | Catalyst (g) | | reaction time on stream (h) | feed flow (cm^3/min) | reaction temperature (°C) | pressure, P (bar) | reactor recycle ratio | SC i-C$_4$ flow (cm^3/min)^a |
	RXT1	RXT2						
synthetic	2.007	2.005	3.0	0.25	60	111	180−200	2.00
commercial	2.008	2.005	3.0	0.25	60	111	200−240	2.00
commercial	2.003	2.002	2.0	0.25	60	111	200−240	2.00

^{a} Supercritical isobutane (regenerant) flow rate.

Table 3. Reaction and Regeneration Cycle Times for the Alkylation Reaction and Isobutane Regeneration Steps^a

| feed blend | reaction time (min) | regeneration cycle time (min)^b | Regeneration Cycle Step Times | | | | |
			reactor purge time (min)	heat time (min)	supercritical fluid (SCF) regeneration time (min)	cool time (min)	hold time (min)
synthetic	180	180	10	30	120	5	15
commercial	180	180	10	30	120	5	15
commercial	120	120	10	30	60	5	15

^{a} Alkylation reaction steps were performed at 60 °C and 111 bar, while regeneration was performed at 180 °C and 111 bar using supercritical isobutane. Control experiments comprised of a single reaction step without regeneration were also performed at 60 °C and 111 bar, ending when TMP products were no longer observed in the reactor effluent. ^{b} Total regeneration cycle time including reactor purge, heating to 180 °C, SCF regeneration at 180 °C, cooling to 60 °C in preparation for the next reaction step, and hold time at 60 °C while waiting for the reaction step proceeding in the parallel swing column to complete.

Supelco Petrocol GC column (Bellefonte, PA) at a split ratio of 100:1. The oven temperature was held initially at 50 °C for 5 min, ramped to 150 °C at 10 °C/min, and held at 150 °C for 0.5 min. Helium carrier gas was maintained at a constant linear velocity of 36 cm/s. FID peaks were identified by comparison with a qualitative reference alkylate standard (Supelco) that was analyzed under identical conditions.

The GC method was purposely kept short to maximize analysis of the transient catalyst activity; however, this limited product analysis such that 2,5-dimethylhexane (2,5-DMH) and 2,2,3-trimethylpentane (2,2,3-TMP) were not separated and hydrocarbons with more than 12 carbons (C$_{12+}$) were not quantified. Because the 2,5-DMH and 2,2,3-TMP peaks were not separated, we assigned that overlapped peak to 2,5-DMH, to be conservative in our product quality analysis.

2.5. Alkylation Reaction and Catalyst Regeneration Conditions. Experiments were performed to assess the efficacy of the supercritical isobutane regeneration process for partially deactivated USY catalyst in the automated system using both preblended synthetic and commercial alkylation feeds. Conditions and times for the alkylation reaction and isobutane regeneration steps were specified based on previous results obtained in a manual reaction/regeneration system.[16] Reaction and regeneration conditions are shown in Table 2, whereas reaction and regeneration cycle times are shown in Table 3.

Control experiments were performed with each feed to determine the maximum catalyst lifetime without supercritical isobutane regeneration. In these experiments, the system was operated with a single reactor and the catalyst was not regenerated. The reaction was run for 24 h with each feed blend after which time the alkylation activity of the catalyst declined significantly. Because of equipment and budget constraints, the nonregeneration experiment using the synthetic feed was performed at a lower recycle ratio than the remaining experimental matrix and, therefore, should be viewed only as a qualitative indicator.

In the supercritical isobutane regeneration process, the amount of catalyst deactivation that is allowed to occur before the catalyst is regenerated has a strong effect on the overall catalyst longevity.[16] In the first and second reaction/regeneration experiments, which used synthetic and commercial alkylation feed blends, respectively, a reaction time of 3 h was utilized, with a 2 h supercritical (SC) regeneration time (time at regeneration temperature). The total regeneration cycle time was 3 h, which included flushing the reactants and products from the reactor with isobutane at the reaction temperature and ramping the temperature to the regeneration temperature before the regeneration, as well as decreasing the temperature back to the reaction temperature after the regeneration. In the third experiment, the system was tested using the commercial feed blend with a reaction time of 2 h and a SC regeneration time (at regeneration temperature) of 1 h, and a total regeneration cycle time of 2 h.

2.6. Data Analysis. Yields of products from the reaction were calculated by integrating the production rate versus time data for each run. The production rates (in terms of grams per hour (g/h)) were calculated from the feed input rate (g/h) and the product weight fraction (in terms of weight percent (wt %)) and plotted versus time. The integrals were normalized, for comparison, by dividing by the total weight of catalyst in the reactor. The percentage of activity recovered was calculated by dividing the yield after deactivation/regeneration by the yield from the fresh catalyst and multiplying the result by 100%.

3. Results

The automated alkylation/regeneration system was constructed and tested initially with the synthetic alkylation feed blend. Testing was performed using an alkylation reaction time on stream (TOS) of 3 h, with a 3 h regeneration cycle that included 2 h at the regeneration temperature of 180 °C. The automated reaction/regeneration system was operated in this manner until the butene conversion dropped below 92%. The actual butene conversion at which the test was stopped was 91.8%, at the end of the 35th cycle (35 alkylation steps for each of the two reactors). Testing then focused on the commercial feed blend, using identical reaction and regeneration cycle times, and the same stop criterion for the test except that the alkene conversion was used as the stop criterion for the test. The actual alkene conversion at which the test was stopped was 92.0%, at the end of the 13th cycle. The faster drop in alkene conversion was attributed to a more-rapid formation of fouling compounds on the surface of the catalyst using the commercial feed. Hence, another test was performed using a shorter reaction step (2 h) and a correspondingly shorter regeneration cycle (2 h, with 1 h at 180 °C). This test was also stopped when the alkene conversion dropped below 92%. The actual alkene conversion at which the test was stopped was 91.4%, at the end of the 48th cycle. The results of each test case are presented in the following sections.
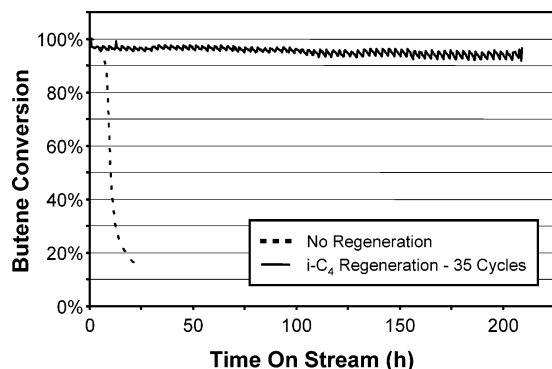
Figure 2. Variation of the butene conversion with the time on stream using the synthetic feed. Included are the synthetic feed regenerated experiment, using a reaction time of 3 h and regeneration cycle time of 3 h (2 h at 180 °C), and the nonregenerated synthetic feed experiment.
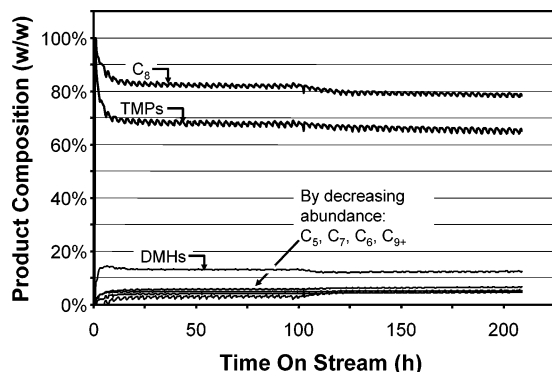

Figure 3. Product composition (given in units of wt %) as a function of the time on stream for alkylation using the synthetic feed with a reaction time of 3 h and regeneration cycle time of 3 h (2 h at 180 °C).

3.1. Synthetic Feed Blend Tests. 3.1.1. Butene Conversion. The time course of butene conversion for the automated reaction/ regeneration system using the synthetic feed blend is shown in Figure 2. Also included is the time course of butene conversion utilizing a single reactor without regenerating the catalyst. This deactivation test was conducted for 24 h, at which time it was clear from the GC analyses that primarily butene dimerization products were being produced by the catalyst (not shown). Butene conversion in the nonregenerated experiment decreased below 92% after ~7.0 h and then decreased very rapidly below 40% after ~11 h. No TMP products were observed in the system outlet after 12.31 h. As mentioned previously, because of equipment issues, a lower recycle ratio was used for the experiment without regeneration and results should only be considered qualitative.

In contrast, in the 3 h alkylation/3 h regeneration test, the butene conversion did not drop below 92% until the end of the 35 reaction/regeneration cycles, corresponding to 210 h of semicontinuous reactor operation divided between the two swing reactors. The butene conversion decreased slightly over the course of each run, indicating that deactivation occurred during each alkylation run. The rate of change of the average butene conversion observed during each successive reaction step (70 total runs) was approximately −0.051%/run, whereas the rate of decrease of the minimum observed butene conversion in the runs was approximately −0.067%/run.

3.1.2. Alkylate Composition. The alkylate composition (total alkylate basis) is plotted in Figure 3 as a function of TOS for the automated reaction/regeneration system using the synthetic feed blend with a reaction time of 3 h and regeneration cycle time of 3 h (2 h at 180 °C). The initial fractions of the alkylate represented by C_8 hydrocarbons and TMPs were initially near
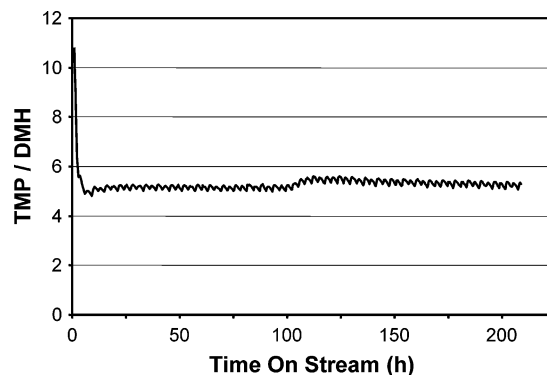

Figure 4. Variation of the trimethylpentane/dimethylhexane (TMP/DMH) ratio, as a function of the time on stream for alkylation using the synthetic feed with a reaction time of 3 h and regeneration cycle time of 3 h (2 h at 180 °C).

theoretical but decreased to ~84 wt % and 70 wt %, respectively, after ~11 h on stream. This occurred because the system, including the recycle loop, was initially filled with isobutane and, thus, the isoparaffin:olefin ratio was initially very high but slowly decreased to the feed blend value of 20.5 over this time period. Hence, subsequent calculations of product yields and catalyst activity recoveries were normalized to the values at 11 h on stream for comparison. In addition, product compositions were considered only after this time point (runs 4−70).

The average C_8 and TMP compositions exiting the reactor system after system stabilization (cycles 2−35) were 80.7 ± 3.4 wt % and 67.0 ± 2.7 wt %, respectively (all variances presented are ±2 standard deviations). The C_8 and TMP compositions decreased slowly with successive reaction steps, reaching ~78 wt % and ~65 wt % after 35 reaction/regeneration cycles (Figure 3). The rates of decline in the average C_8 and TMP compositions over the test were −0.082 wt %/run and −0.060 wt %/run, respectively, after system stabilization.

Products from side reactions and cracking (C_{5+}, exclusive of C_8 hydrocarbons) comprised an average of 15.7 wt % of the alkylate after the system stabilized (run 4), with average run 4 compositions of 5.3 wt % C_5, 3.6 wt % C_6, 4.7 wt % C_7, and 2.1 wt % C_{9+} products. The average run 70 compositions were 6.6 wt % C_5, 4.7 wt % C_6, 5.3 wt % C_7, and 5.0 wt % C_{9+} products. The overall rate of increase in these products in the alkylate (C_{5+}, exclusive of C_8 hydrocarbons) was 0.082 wt %/run, including 0.017 wt %/run for C_5, 0.012 wt %/run for C_6, 0.008 wt %/run for C_7, and 0.045 wt %/run for C_{9+}.

The run-averaged DMH composition stabilized by approximately run 4 as the product composition stabilized (see Figure 3), at a value of 13.7 wt %, and decreased to 12.3 wt % by run 70, an average decline rate of −0.021 wt %/run. The ratio of TMPs to DMHs in the automated swing column reactor system is shown in Figure 4. The average TMP/DMH ratio stabilized initially at 5.08 (run 4) and then slowly increased at an average rate of 3.94×10^{-3} per run to a run 70 average ratio of 5.30. As observed previously for the alkylate composition results, the initial TMP/DMH ratio was ~11 and decreased rapidly to a stabilized value of 5.08 (run 4). This was the result of the experimental startup procedure where the entire system, including the recycle loop, was filled with isobutane, providing a isoparaffin:olefin ratio that was initially very high but decreased to the feed blend value of 20.5 over the start-up period.

3.1.3. Alkylate and Trimethylpentane Yields. The C_{5+} and TMP product yields (given in terms of grams of product per gram of catalyst per hour) are presented in Figure 5 as functions
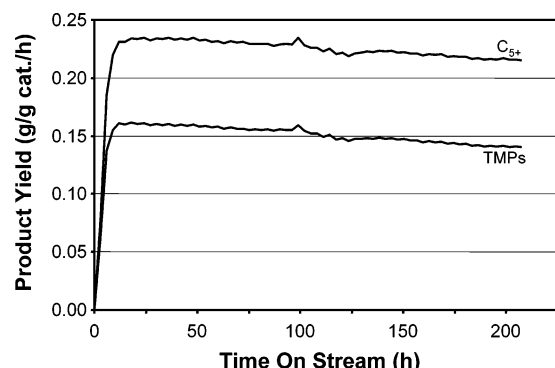
Figure 5. Product yield for the swing column system (given in units of g product/g catalyst/h) as a function of the time on stream for alkylation using the synthetic feed with a reaction time of 3 h and regeneration cycle time of 3 h (2 h at 180 °C).
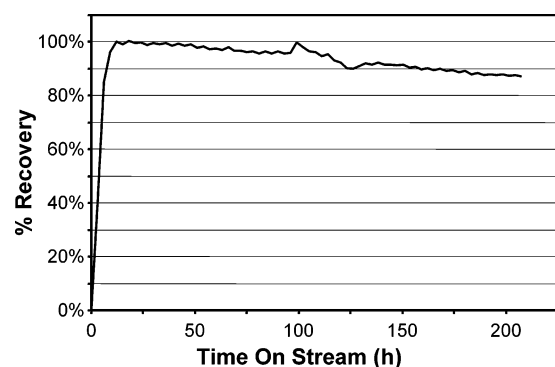

Figure 6. Percentage recovery of TMP yield per gram of catalyst for the swing column system as a function of the time on stream for alkylation using the synthetic feed with a reaction time of 3 h and regeneration cycle time of 3 h (2 h at 180 °C). The recovery of activity is normalized to the yield observed for run 4, which accounts for the start-up effects of system volume on the measured product compositions.

of the TOS for the alkylation/regeneration using the synthetic feed. During stabilization of the reactor inlet feed composition, the yields rapidly increased to values of 0.220 g C_{5+}/g catalyst/h and 0.155 g TMP/g catalyst/h, respectively, at the conclusion of run 4. The yields were maintained near this level over the course of the 35 reaction/regeneration cycles (70 total runs), with yields of 0.215 g C_{5+}/g catalyst/h and 0.140 g TMP/g catalyst/h for run 70, respectively. The rates of decline of the yields averaged -3.18×10^{-4} g C_{5+}/g catalyst/h/run and -3.49×10^{-4} g TMP/g catalyst/h/run, respectively, over this period. The yields averaged over runs 4−70 were 0.225 ± 0.013 g C_{5+}/g catalyst/h and 0.151 ± 0.014 g TMP/g catalyst/h, respectively.

Note that, after ∼100 h of TOS, the pump supplying isobutane for supercritical regeneration experienced significant operational difficulties, resulting in impaired flow of the regeneration fluid. The issue was resolved within ∼24 h; however, during this time period, product yields declined at a rate greater than that for the rest of the experiment. Following restoration of stable regenerate fluid flow operation, the rate of decline of the yields was again lower.

3.1.4. Maintenance of Alkylation Activity. The percentage recovery of TMP yield per gram of catalyst is shown in Figure 6 as a function of the TOS for the alkylation/regeneration using the synthetic feed. The percentage activity recoveries were calculated for a given alkylation step (run) by dividing the TMP yield for that run by an initial TMP activity. Because the system needed 11 h to stabilize the reactor inlet feed compositions (because of the system initially being filled with isobutane),
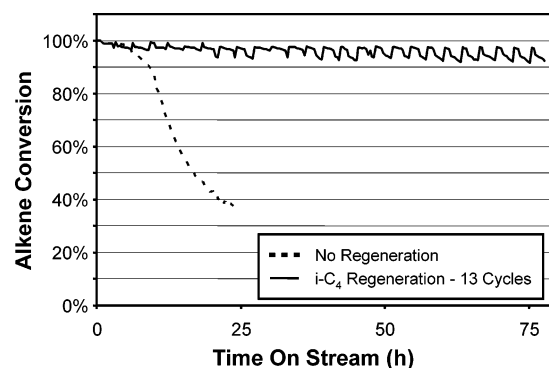

Figure 7. Variation of alkene conversion with the time on stream using the commercial feed. Included are the commercial feed control (non-regenerated) and commercial feed regenerated experiment using a reaction time of 3 h and regeneration cycle time of 3 h (2 h at 180 °C).

the TMP yield for run 4 (9−12 h) was chosen as the appropriate "initial" yield for the normalization; hence, the normalized percentage TMP activity recovery beginning with run 4 is 100%. This normalization accounts for the start-up effects of system volume on the measured product compositions.

By the end of the experiment (run 70), the percentage of TMP activity recovered in the last run was 87.2% of the yield observed for run 4. The run 70 C_{5+} activity recovery was 93.3% of the run 4 value (not shown). The TMP activity recovery declined at an average rate of −0.216%/run from run 4 to run 70, whereas the C_{5+} activity decreased by an average of −0.137%/run over the same period (not shown).

As stated previously, after ∼100 h of TOS, the pump that supplied isobutane for the SC regeneration experienced significant operational difficulties. However, the issue was resolved: during this time period, activity recovery declined at a rate greater than that for the rest of the experiment. Following restoration of stable fluid flow, the rate of decline of activity recovery was again lower.

3.2. Commercial Feed Blend Tests. 3.2.1. 3-h Alkylation Runs. 3.2.1.1. Alkene Conversion. The time course of alkene conversion for the automated reaction/regeneration system using the commercial feed blend with a reaction time of 3 h and a regeneration cycle time of 3 h (2 h at 180 °C) is shown in Figure 7. Also included is the time course of alkene conversion utilizing a single reactor without regenerating the catalyst. As previously done for the synthetic feed blend, the control deactivation test was run for 24 h. Alkene conversion in the nonregenerated control decreased to below 92% after ∼8.3 h and then decreased very rapidly to below 40% after ∼22 h.

In contrast, in the 3 h alkylation/3 h regeneration test, the alkene conversion remained at or above 92% for 13 reaction/regeneration cycles, corresponding to 78 h of semicontinuous reactor operation divided between the two swing reactors. The alkene conversion decreased slightly over the course of each run, indicating that deactivation occurred during each alkylation run. The rate of change of the average alkene conversion observed during each successive reaction step (26 total runs) was approximately −0.150%/run, whereas the rate of decrease of the minimum observed alkene conversion in the runs was approximately −0.207%/run.

3.2.1.2. Alkylate Composition. The alkylate composition (total alkylate basis) is plotted in Figure 8 as a function of the time on stream for the automated reaction/regeneration system using the commercial feed blend with a reaction time of 3 h and regeneration cycle time of 3 h (2 h at 180 °C). The initial fractions of the alkylate represented by C_8 hydrocarbons and TMPs were initially higher but decreased to ∼55 wt % and
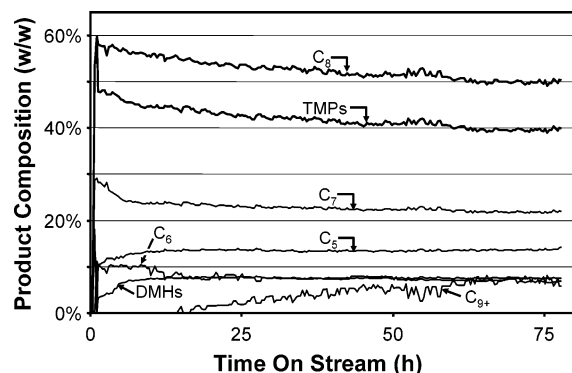
Figure 8. Product composition (given in units of wt %) as a function of the time on stream for alkylation using the commercial feed with a reaction time of 3 h and regeneration cycle time of 3 h (2 h at 180 °C).
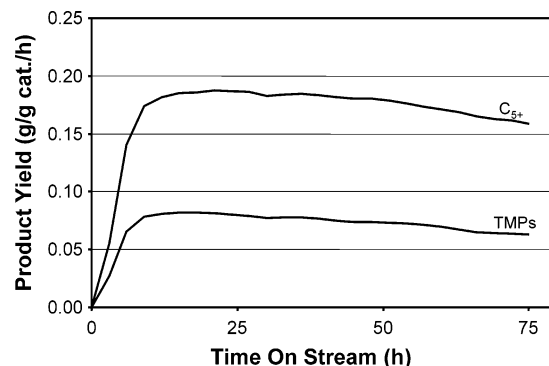

Figure 9. Product yield for the swing column system (given in units of g product/g catalyst/h) as a function of the time on stream for alkylation using the commercial feed with a reaction time of 3 h and regeneration cycle time of 3 h (2 h at 180 °C).
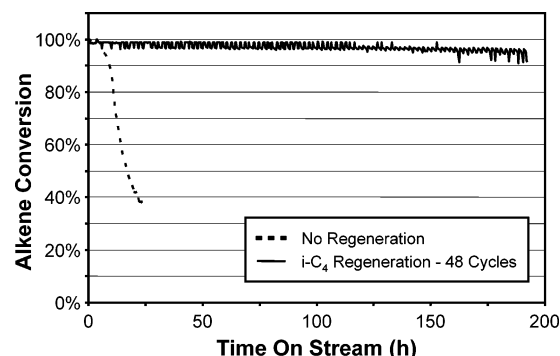

Figure 10. Variation of alkene conversion with the time on stream using the commercial feed. Included are the commercial feed control (non-regenerated) and commercial feed regenerated experiment, using a reaction time of 2 h and regeneration cycle time of 2 h (1 h at 180 °C).

~45 wt %, respectively, after ~11 h on stream. As with the synthetic feed tests, this occurred because the system, including the recycle loop, was initially filled with isobutane and, thus, the isoparaffin:olefin ratio was initially very high but slowly decreased to the feed blend value of 21.6 over this time period. Hence, subsequent calculations of product yields and catalyst activity recoveries were normalized to the values at 11 h on stream for comparison. In addition, product compositions were considered only after this time point (runs 4−26).

After the reactor inlet feed composition stabilized, the C_8 and TMP compositions decreased slowly with successive reaction steps, reaching ~50 wt % and ~40 wt % after 13 reaction/regeneration cycles (see Figure 8). The rates of decline in the average C_8 and TMP compositions over the test were −0.247 wt %/run and −0.226 wt %/run, respectively, after system stabilization.

Other non-C_8 alkylation products include C_7, C_9, and C_{10} products from the alkylation of isobutane with propylene (C_7) or pentenes (C_9), and from the alkylation of isopentane with butenes (C_9) and pentenes (C_{10}). The greatest amounts of non-C_8 alkylation products would be expected to be C_7 compounds: the commercial feed blend (see Table 1) contained 8 times more propylene than pentenes (by weight; ~13.8 times more, in terms of moles), and 382 times more isobutane than isopentane (by weight; ~474 times more, in terms of moles). Additional non-C_8 products would include products from side reactions and cracking products.

The total composition of non-C_8 products, which includes all of the classes of products described previously, comprised an average of 44.4 wt % of the alkylate after the system stabilized (run 4), consisting of average run 4 compositions of 13.3 wt % C_5, 7.4 wt % C_6, 23.7 wt % C_7, and 0.0 wt % C_{9+} products (Figure 8). The average run 26 compositions of these were 13.8 wt % C_5, 7.5 wt % C_6, 21.9 wt % C_7, and 6.8 wt % C_{9+} products. The overall rate of increase in these products in the alkylate (C_{5+}, exclusive of C_8 hydrocarbons) was 0.247 wt %/run, including 0.008 wt %/run for C_5, −0.005 wt %/run for C_6, −0.087 wt %/run for C_7, and 0.331 wt %/run for C_{9+}.

The run-averaged DMH composition stabilized (see Figure 8) at a value of 9.1 wt % and decreased to 6.7 wt % by run 26, an average decline rate of −0.060 wt %/run. The average TMP/DMH ratio (not shown) stabilized initially at ~5.47 during run 5 and slowly increased at an average rate of 0.0129 per run to a run 26 average ratio of 5.88.

3.2.1.3. Alkylate and Trimethylpentane Yields. The C_{5+} and TMP product yields (in units of g product/g catalyst/h) are presented in Figure 9 as functions of the time on stream for the

alkylation/regeneration. During stabilization of the reactor inlet feed composition, the yields rapidly increased to values of 0.181 g C_{5+}/g catalyst/h and 0.081 g TMP/g catalyst/h, respectively, at the conclusion of run 4. The yields were maintained near this level over the course of the 13 reaction/regeneration cycles (26 total runs), with yields of 0.151 g C_{5+}/g catalyst/h and 0.060 g TMP/g catalyst/h for run 26, respectively. The rates of decline of the yields averaged -1.26×10^{-3} g C_{5+}/g catalyst/h/run and -9.35×10^{-4} g TMP/g catalyst/h/run, respectively, over this period.

3.2.2. 2-h Alkylation Runs. 3.2.2.1. Alkene Conversion. The time course of alkene conversion for the automated reaction/regeneration system using the commercial feed blend with a reaction time of 2 h and a regeneration cycle time of 2 h (1 h at 180 °C) is shown in Figure 10. Also included is the time course of alkene conversion utilizing a single reactor without regenerating the catalyst, which is the same control (no regeneration) experiment as that plotted in Figure 7. (Refer to the appropriate section presented previously, along with Figure 7, for the results of the control experiment.)

In the 2 h alkylation/2 h regeneration test, the alkene conversion dropped below 92% at the end of 48 reaction/regeneration cycles, corresponding to 192 h of semicontinuous reactor operation divided between the two swing reactors. The alkene conversion decreased slightly over the course of each run, indicating that deactivation occurred during each alkylation run. The rate of change of the average alkene conversion observed during each successive reaction step (96 total runs) was approximately −0.035%/run, whereas the rate of decrease of the minimum observed alkene conversion in the runs was approximately −0.041%/run.
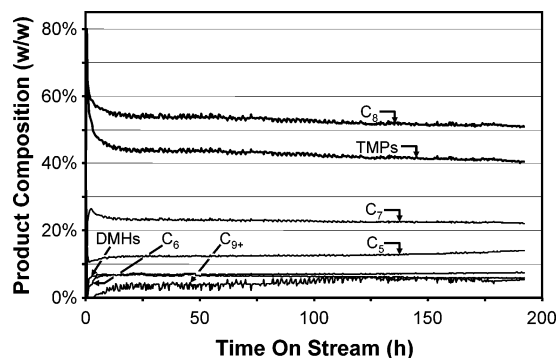
Figure 11. Product composition (given in units of wt %) as a function of the time on stream for alkylation using the commercial feed with a reaction time of 2 h and regeneration cycle time of 2 h (1 h at 180 °C).

3.2.2.2. Alkylate Composition. The alkylate composition (total alkylate basis) is plotted in Figure 11 as a function of the time on stream for the automated reaction/regeneration system using the commercial feed blend with a reaction time of 2 h and regeneration cycle time of 2 h (1 h at 180 °C). The initial fractions of the alkylate represented by C_8 hydrocarbons and TMPs were initially higher but stabilized after ∼11 h on stream to ∼55 wt % and ∼45 wt %, respectively. As previously described, subsequent calculations of product yields and catalyst activity recoveries were normalized to the values at 11 h on stream for comparison. In addition, product compositions are discussed only after this time point (runs 6−96).

After the reactor inlet feed composition stabilized, the C_8 and TMP compositions decreased slowly with successive reaction steps, reaching ∼51 wt % and ∼40 wt %, respectively, after 48 reaction/regeneration cycles (see Figure 11). The rates of decline in the average C_8 and TMP compositions over the test were −0.040 wt %/run and −0.042 wt %/run, respectively, after system stabilization.

As observed with the 3 h reaction/3 h regeneration cycle test using the commercial feed blend, other non-C_8 alkylation products for the 2 h reaction/2 h regeneration cycle test would include C_7, C_9, and C_{10} products from the alkylation of isobutane with propylene (C_7) or pentenes (C_9), and from the alkylation of isopentane with butenes (C_9) and pentenes (C_{10}). The greatest amounts of non-C_8 alkylation products would again be expected to be C_7 compounds. Additional non-C_8 products would include products from side reactions and cracking products.

The total composition of non-C_8 products, which includes all of the classes of products described in the previous paragraph, comprised an average of 45.1 wt % of the alkylate after the system stabilized (run 6), consisting of average run 6 compositions of 12.0 wt % C_5, 6.7 wt % C_6, 23.6 wt % C_7, and 2.8 wt % C_{9+} products (see Figure 11). The average run 96 compositions of these were 14.0 wt % C_5, 7.5 wt % C_6, 22.1 wt % C_7, and 5.4 wt % C_{9+} products. The overall rate of increase in these products in the alkylate (C_{5+}, exclusive of C_8 hydrocarbons) was 0.040 wt %/run, including 0.017 wt %/run for C_5, 0.006 wt %/run for C_6, −0.013 wt %/run for C_7, and 0.030 wt %/run for C_{9+}.

The run-averaged DMH composition stabilized by approximately run 6 as the product composition stabilized (see Figure 11), at a value of 6.8 wt %, and decreased to 5.9 wt % by run 96, at an average rate of decline of −0.012 wt %/run. The average TMP/DMH ratio (not shown) stabilized initially at ∼6.61 during run 5 and slowly increased at an average rate of 6.47×10^{-3} per run to a run 96 average ratio of 6.75. The average DMH composition and TMP/DMH ratio in the stream
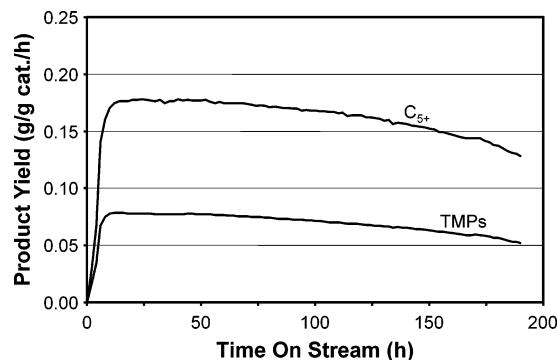

Figure 12. Product yield for the swing column system (given in units of g product/g catalyst/h) as a function of the time on stream for alkylation using the commercial feed with a reaction time of 2 h and regeneration cycle time of 2 h (1 h at 180 °C).
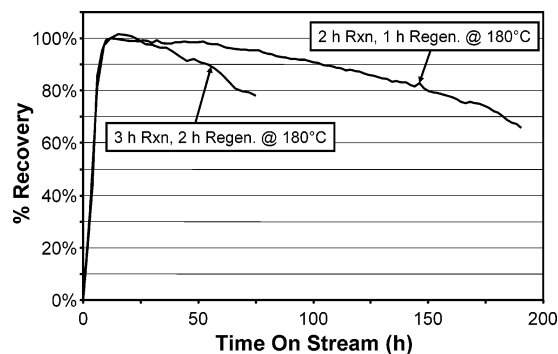

Figure 13. Percentage recovery of TMP yield per gram of catalyst for the swing column system as a function of the time on stream for alkylation using the commercial feed with reaction times of 2 or 3 h and regeneration cycle times of 2 or 3 h (1 h or 2 h at 180 °C), respectively. The recoveries of activity are normalized to the yields observed in the first run in each test in which the reactor inlet feed compositions were stabilized, which accounts for the start-up effects of system volume on the measured product compositions.

exiting the reactor system after stabilization were 6.3 ± 0.7 wt % and 6.75 ± 0.46, respectively.

3.2.2.3. Alkylate and Trimethylpentane Yields. The C_{5+} and TMP product yields (given in units of g product/g catalyst/h) are presented in Figure 12 as functions of the time on stream for the alkylation/regeneration using the commercial feed with 2 h reaction and 2 h regeneration cycle times. During stabilization of the reactor inlet feed composition, the yields rapidly increased to values of 0.175 g C_{5+}/g catalyst/h and 0.079 g TMP/g catalyst/h, respectively, at the conclusion of run 6. The yields slowly decreased from this level over the course of the 48 reaction/regeneration cycles (96 total runs), with yields of 0.128 g C_{5+}/g catalyst/h and 0.052 g TMP/g catalyst/h for run 96, respectively. The rates of decline of the yields averaged -5.03×10^{-4} g C_{5+}/g catalyst/h/run and -2.82×10^{-4} g TMP/g catalyst/h/run rate, respectively, over this period.

3.2.2.4. Maintenance of Alkylation Activity. The percentage recovery of TMP yield per gram of catalyst is shown in Figure 13 as a function of the time on stream for the alkylation/ regeneration using the commercial feed blend. For comparison, data are shown for both the 3 h reaction/3 h regeneration cycle test and the 2 h reaction/2 h regeneration cycle test. As done previously for the synthetic feed blend test, the percentage activity recoveries were calculated for a given run by dividing the TMP yield for that run by an initial TMP activity. Because the system required 11 h to stabilize the reactor inlet feed compositions, the TMP yield for run 4 (9−12 h) was chosen as the appropriate "initial" yield for the normalization for the 3 h

Table 4. Comparison of Productive Time-on-Stream, Cumulative Yields, and C_{5+} and TMP Productivities for the Control (No Regeneration), 3 h Reaction/3 h Regeneration Cycle Tests, and 2 h Reaction/2 h Regeneration Cycle Tests, Using the Commercial Feed Blend. Two Criteria for Ending the Test Are Presented: (1) Loss of 8 % of the Alkene Conversion and (2) Loss of 10% of the TMP Activity

test result	no regeneration control	3 h reaction/3 h regeneration cycle	2 h reaction/2 h regeneration cycle
	Criterion 1: Stop Test at 92% Alkene Conversion		
time on stream, TOS	8.34 h	77.79 h	192.3 h
cumulative C_{5+} yield	1.303 g/g catalyst	13.25 g/g catalyst	30.72 g/g catalyst
cumulative TMP yield	0.601 g/g catalyst	5.564 g/g catalyst	13.15 g/g catalyst
C_{5+} productivity	0.156 g/g catalyst/h TOS	0.170 g/g catalyst/h TOS	0.160 g/g catalyst/h TOS
TMP productivity	0.0720 g/g catalyst/h TOS	0.0715 g/g catalyst/h TOS	0.0684 g/g catalyst/h TOS
	Criterion 2: Stop Test when 90% TMP Activity Remains		
time on stream, TOS	3.33 h	57.09 h	104.2 h
cumulative C_{5+} yield	0.251 g/g catalyst	9.88 g/g catalyst	17.52 g/g catalyst
cumulative TMP yield	0.130 g/g catalyst	4.22 g/g catalyst	7.67 g/g catalyst
C_{5+} productivity	0.0754 g/g catalyst/h TOS	0.173 g/g catalyst/h TOS	0.168 g/g catalyst/h TOS
TMP productivity	0 0.0392 g/g catalyst/h TOS	0.0740 g/g catalyst/h TOS	0.0736 g/g catalyst/h TOS

reaction case, while the TMP yield for run 6 (10−12 h) was chosen as the appropriate "initial" yield for the normalization for the 2 h reaction case.

For the 3 h reaction/3 h regeneration cycle (2 h at 180 °C) test (see Figure 13), by the end of the experiment (run 26), the percentage of TMP activity recovered in the last run was 77.9% of the yield observed for run 4. The C_{5+} activity recovery was 87.8% of the run 4 value (not shown). The TMP activity recovery declined at an average rate of −1.156%/run from run 4 to run 26, whereas the C_{5+} activity decreased by an average of −0.692%/run over the same period (not shown). For the 2 h reaction/2 h regeneration cycle (1 h at 180 °C) test, by the end of the experiment (run 96), the percentage of TMP activity recovered in the last run was 65.9% of the yield observed for run 6. The C_{5+} activity recovery was 73.1% of the run 6 value (not shown). The TMP activity recovery declined at an average rate of −0.358%/run from run 6 to run 96, whereas the C_{5+} activity decreased by an average of −0.288%/run over the same period (not shown). The shorter 2 h reaction/2 h regeneration test fared better, with respect to both C_{5+} and TMP activity recovery, than did the 3 h/3 h test, giving significantly more reaction cycles and a greater total time on stream. It is notable that the TMP activity remaining at the end of the tests (i.e., at ca. 90% alkene conversion; see Figures 7 and 10) was much lower for the 2 h/2 h test (65.9%) than was observed in the 3 h/3 h test (77.9%).

3.2.2.5. Product Yields and Productivity Using the Commercial Feed Blend. The productive times on stream, cumulative yields, and C_{5+} and TMP productivities (defined as the product yield per gram of catalyst divided by the total TOS)
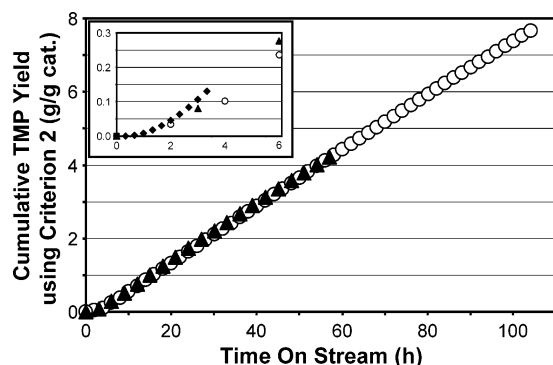

Figure 14. Cumulative TMP yields from alkylation of the commercial feed blend as a function of the time on stream using criterion 2 (the loss of 10% of the initial TMP activity) to determine when the test is ended. Legend is as follows: (◆) non-regenerated control, (▲) swing column system with a reaction time of 3 h and a regeneration cycle time of 3 h, and (○) swing column system with a reaction time of 2 h and a regeneration cycle time of 2 h (1 h at 180 °C). The inset shows the control data in its entirety.

are compared in Table 4 for the control (no regeneration), 3 h reaction/3 h regeneration cycle tests, and 2 h reaction/2 h regeneration cycle tests, using the commercial feed blend. Two criteria for ending the test are shown: (1) the loss of a predetermined amount of the alkene conversion, set here as ca. 8%, because that is the point at which the regeneration tests were terminated (92% alkene conversion); and (2) the loss of 10% of the TMP activity.

When an 8% loss of alkene conversion was used as the criterion for comparison, the regenerated swing reactors combined for increases in the productive time on stream by factors of 9.3 and 23.1 for the 3 h/3 h and 2 h/2 h tests, respectively, versus the nonregenerated control case. The cumulative C_{5+} and TMP yields were increased by factors of 10.2 and 9.3, respectively, for the 3 h reaction/3 h regeneration cycle test and increased by factors of 23.6 and 21.9, respectively, for the 2 h reaction/2 h regeneration cycle test. The C_{5+} and TMP productivities were essentially unchanged for both regenerated tests versus the control, with slight increases for C_{5+} and slight decreases for TMPs for both regenerated cases.

When a 10% loss of TMP activity was used as the criterion for comparison, the regenerated swing reactors combined for increases in the productive time on stream by factors of 17.1 and 31.3 for the 3 h/3 h and 2 h/2 h tests, respectively, versus the nonregenerated control case. The cumulative C_{5+} and TMP yields were increased by factors of 39.3 and 32.4, respectively, for the 3 h reaction/3 h regeneration cycle test and increased by factors of 69.7 and 58.8, respectively, for the 2 h reaction/2 h regeneration cycle test. Using this criterion, the C_{5+} productivities increased by a factor of ~2.2 versus the control productivity for the two regenerated cases. The TMP productivities increased by a factor of ~1.9 versus the control productivity for both regenerated cases.

Using the second criterion (stopping the test after a 10% loss of the initial TMP activity), the time courses of the cumulative TMP yields are shown in Figure 14 for the tests utilizing the commercial feed blend. The inset in Figure 14 shows the control data in its entirety. The rates of TMP production for the three cases track each other reasonably closely in the overlapping ranges of TOS. Hence, the net effect of the regeneration was to extend the active catalyst lifetime, thereby allowing higher yields per unit of catalyst.

4. Discussion

The purpose of this effort was to explore the effectiveness of supercritical isobutane for multiple regenerations of a solid acid catalyst used in isoparaffin alkylation. This effort was constrained to that purpose, and the exploration of improved

catalysts, reaction conditions, and regeneration conditions was not investigated here. In addition, the experimental efforts in this study were limited to fixed-bed, semicontinuous reaction/regeneration cycles. Note that other continuous reaction and regeneration methods using supercritical isobutane could be used. Although improved catalysts and reactor design are desired, the results from this study demonstrated that, for both synthetic and commercial feeds, supercritical isobutane regeneration is highly effective at maintaining catalyst longevity.

In our prior studies, we have shown that supercritical isobutane regeneration is a reactive regeneration process.[13] In that work, it was shown that the supercritical isobutane regenerates the catalyst by first facilitating hydride transfer to the surface adsorbed deactivating carbonaceous species and then aiding its removal from the porous catalyst matrix via supercritical extraction. The process not only cleans the catalyst surface, restoring surface area, catalyst acidity, and acid site accessibility,[15] but also leaves an isobutane carbocation on the catalyst surface, such that the reaction rates, product yields and product quality are improved after regeneration, compared to the fresh catalyst.[17] We further demonstrated that the regeneration process was not significantly affected by regeneration pressures between 42 and 139 bar, such that much-lower regeneration pressures than those reported in this work are possible.[14] Although not investigated in this paper, because of experimental and analytical equipment constraints, our prior work[14] found that (i) during the purge and heating portions of the regeneration step, the hydrocarbons that issued from the catalyst bed were simply the alkylate products, and (ii) during the supercritical regeneration step, only TMPs were detected. Thus, it may be possible for the regenerant fluid to be recycled directly into the reaction feed stream with no, or only minimal, cleanup.

Synthetic feed experiments showed that high levels of butene conversion were maintained for more than 200 h on stream, and that product quality and catalyst maintenance were relatively stable over the course of the experiment. As reported earlier, TMP/DMH quality improved slightly over the course of the run, possibly because of changes in the alkylation initiation step,[18,19] isomerization rates,[4,20] and the decrease in catalyst pore size, leading to changes in restricted diffusion rates.[4,19] A more-detailed discussion of these influences can be found elsewhere.[17]

Commercial feed experiments had notably more moderate, but still significant, benefits. As expected, the C_8 product fraction was lower at the expense of primarily C_7 products, compared to the synthetic feed results. This shift was due to the presence of C_3 and C_5 olefins and lower concentrations of C_4 olefins in the commercial feed blend. In addition, C_5 compounds quantified in the product were higher in the commercial feed. These compounds may have originated from the feed isopentane because isoparaffins were supplied in excess to the limiting olefin reactants.

More noticeable, however, were the higher levels of activity decline that were observed, especially for the 3 h cycle commercial feed experiments. The diolefins, oxygenates, and sulfur in the commercial feed are well-known catalyst poisons, and their presence significantly enhanced catalyst deactivation and hindered supercritical regeneration. To counter the higher activity degradation, a shorter reaction and regeneration cycle time was used. This change in operating conditions is similar to what is being proposed commercially for solid catalyst isoparaffin alkylation processes. In the developing commercial solid catalyst alkylation processes that rely on hydrogen regeneration,[21] changes in reaction/regeneration cycle time, as well as aggressive feed pretreatment options, are being used to counter the problems with the type of contaminants that are encountered here.

Improved catalyst activity maintenance at shorter times on stream is anticipated, based on our earlier work.[15,17] We recently reported on the effect of supercritical isobutane regeneration on the nature of hydrocarbons on a USY zeolite catalyst used for isobutane/butene alkylation.[15] Alkylation conditions were comparable to those reported here, except that the synthetic feed was investigated at a higher OWHSV. In that work, it was found that as reaction TOS increased, the catalyst surface area and micropore volume decreased due to the adsorption of hydrocarbons primarily present in the supercages of the zeolite structure. The molecular weight of the hydrocarbon species, which were mostly highly branched paraffins, increased with the TOS, and, at longer TOSs, unsaturated cyclic structures were detected by ultraviolet−visible (UV−Vis) spectroscopy on the catalyst surface. The supercritical regeneration process was effective in restoring surface area and micropore volume. It extracted most coke precursors from samples that had been exposed to a short TOS. Samples that were allowed to react for longer TOS may have contained some species, likely cyclic structures that, instead of being extracted by the supercritical fluid, dehydrogenated to produce more-condensed species.

In this work, at the longer reaction time with the commercial feed, it would be expected that higher levels of adsorbed hydrocarbons would result in lower catalyst surface area and micropore volume. Furthermore, the hydrocarbon species would have higher molecular weights and be more dehydrogenated. These species would be more difficult to extract, leading to lower levels of activity recovery. Reducing the reaction time resulted in a subsequently shorter regeneration time. Despite the shorter regeneration time, the shorter cycle provided improved catalyst longevity. This result can be reasonably expected based on our prior work, which found that the majority of activity restoration of completely deactivated USY zeolite alkylation catatlysts by supercritical isobutane occurred during the first 30 min of regeneration.[14]

However, even at the shorter reaction/regeneration cycle time, product production rates were either unchanged (using the alkene conversion criterion; see Table 4) or increased (using the TMP activity criterion; see Table 4), compared to the no regeneration control, while the catalyst lifetimes and product yields were substantially increased using supercritical isobutane regeneration.

5. Conclusions

Supercritical isobutane regeneration is a promising technique for enhancing solid-catalyzed isoparaffin alkylation. For both synthetic and commercial feeds, supercritical isobutane regeneration is highly effective in regard to maintaining catalyst effectiveness and increasing the sustainability of the alkylation reaction. Higher rates of catalyst fouling due to feed contaminants can be accommodated by reducing the reaction cycle time. Although additional work in catalyst development and reactor design is still required before a solid catalyst process can compete with liquid acid process conditions and product quality, supercritical fluid regeneration with isobutane provides a novel method for improving the sustainability of solid alkylation catalysts.

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