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Extended Catalyst Longevity via Supercritical Isobutane Regeneration of a Partially Deactivated USY Alkylation Catalyst

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Off-line, in situ activity recovery of a partially deactivated USY zeolite catalyst used for isobutane/butene alkylation was examined in a continuous-flow reaction system employing supercritical isobutane. Catalyst samples were deactivated in a controlled manner by running them to either a fixed butene conversion level of 95% or a fixed time-on-stream of 3 h and then exposing the catalyst to supercritical isobutane to restore activity. Activity recovery was determined by comparing alkylation activity before and after the regeneration step. Both single and multiple regenerations were performed. Use of a 95% butene conversion level criterion to terminate the reaction step afforded 86% activity recovery for a single regeneration and provided nine sequential reaction steps for the multiple regeneration studies. Employing a fixed, 3 h time-on-stream criterion resulted in nearly complete activity recovery for a single regeneration, and 24 reaction steps were demonstrated in sequence for the multiple regeneration process, producing only minor product yield declines per step. This resulted in a 12-fold increase in catalyst longevity versus unregenerated catalyst.

Introduction

Isoparaffin alkylation is utilized in the petroleum refining industry to produce a low vapor pressure, high-octane gasoline blend stock by coupling high vapor pressure isoalkanes and alkenes. Alkylate is highly desired not only because of its octane rating and blending properties but also because it presents environmental advantages due to its low sulfur, benzene, aromatics, and alkene contents and because it converts undesirable high vapor pressure alkanes and alkenes to a low vapor pressure blend stock. The production of alkylate is necessary to meet U. S. energy demands, and it is considered to be an essential requirement for producing environmentally sound, reformulated gasoline.¹

Current industrial alkylation processes use concentrated mineral acids, including hydrofluoric (HF) or sulfuric acid (H₂SO₄) to catalyze the alkylation reaction.² These processes present serious safety and environmental concerns arising from the need to transport and store the concentrated liquid acids, as well as 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 due primarily to

rapid deactivation from the buildup of coke, difficult catalyst regeneration, poor product quality, and energy-intensive product recovery. The technical 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, rendering the catalyst useless within short periods.^{3,6} Traditional methods of regenerating solid catalysts, such as oxidation and hydrogenation, while generally effective at removing the deposits, often are incomplete,⁷ damage the catalyst,⁸ or require the presence of noble metals in the catalyst and extensive hydrogen supply infrastructure. These factors all serve to significantly increase capital and operating costs.

An alternative 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 supercritical fluids could be used as an off-line, in situ method to regenerate a solid catalyst used in isobutane/butene alkylation.^{12–15} Initially, we reported that a fully deactivated alkylation catalyst could be partially regenerated while a partially deactivated catalyst could be fully regenerated with supercritical fluids.¹² More recently, we examined the choice of supercritical fluid¹³ and the effect of process conditions¹⁴ on regeneration effectiveness for a completely deactivated catalyst. Industrially, catalysts are typically only partially deactivated prior to regeneration; however, in that work we examined regeneration effectiveness employing the severe case of completely deactivated catalysts where

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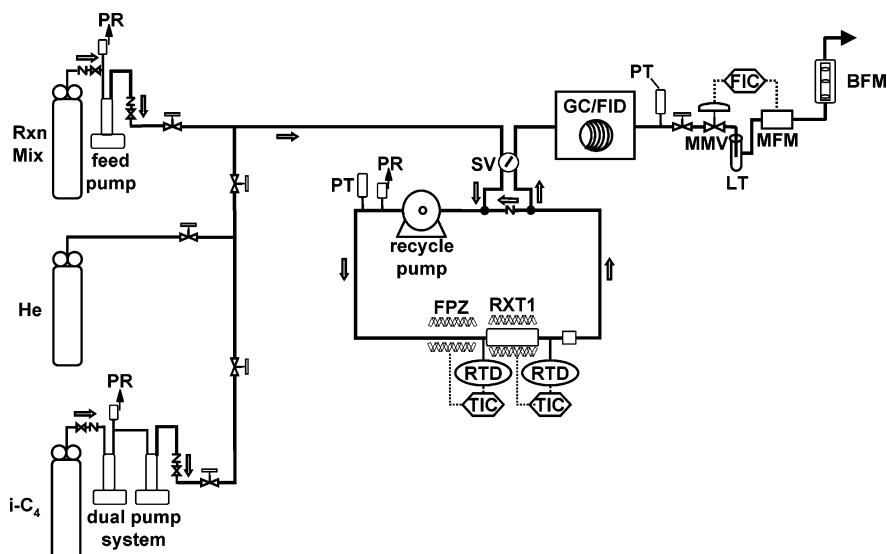


Figure 1. Schematic of the reaction/regeneration system.

the variation among fluids and process conditions was highly apparent.

The purpose of the present study was to explore the effectiveness of supercritical isobutane for multiple regenerations of a solid acid catalyst used in isobutane/butane alkylation. This effort was constrained to that purpose, and the exploration of catalysts, reaction conditions, and regeneration conditions was not conducted here. In this work, we examined catalyst regeneration effectiveness for a partially deactivated catalyst using supercritical isobutane. Two different criteria to end the alkylation reaction and initiate supercritical regeneration were examined: (a) when butene conversion declined to 95% and (b) when a fixed time-on-stream (TOS) was reached. Results are presented for the cases of single regenerations, as well as for multiple regenerations.

Methods

1. Catalysts and Chemicals. An ultrastable Y-zeolite catalyst (USY; Zeolyst International, Valley Forge, PA) was used for the alkylation/reactivation experiments. This catalyst, comprised of 59.8 wt % SiO₂, 39.6 wt % Al₂O₃, and 0.08 wt % Na and having a surface area of 638 m²/g, a pore volume of 0.48 cm³/g, an average pore diameter of 14 Å, and a total acidity of 999 μmol/g, was previously characterized.⁶ 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 with helium (ultrahigh purity (UHP), U.S. Welding, Denver, CO) at 200 °C to remove adsorbed water immediately before use. Failure to perform the drying step resulted in significantly reduced catalyst performance.

Instrument-grade isobutane (99.5%) and high purity (HP)-grade *trans*-2-butene (99.0%) used for the alkylation reaction were obtained from Scott Specialty Gases (Plumsteadville, PA). Instrument-grade isobutane was also used as the supercritical regeneration fluid. Finally, UHP-grade helium (>99.9%) was used to pressure check the reaction system, to purge the system, and to dry the catalysts in the reactor before use.

2. Reactor System. A schematic of a reaction/regeneration system is shown in Figure 1. The basic arrangement of the reactor system utilized in this study

has been previously described.¹³ The reactor system used in the experiments described in this paper was slightly modified from the prior design in that it employed a recycle pump in the reactor loop to approach the performance of a continuous stirred tank reactor (CSTR, Figure 1). In this way, the net isobutane/*trans*-2-butene molar ratio (iP/O) was effectively increased within the reactor, minimizing butene concentration and, thus, improving catalyst stability. In the present system, an Accuflo Series III HPLC pump (Scientific Systems, Inc., State College, PA) that served as a recycle pump was inserted in the reactor loop upstream of the reactor and pressure relief valve (Figure 1). In addition, to accommodate the higher flows within the reactor loop, the reactor diameter was increased to 0.94 cm (i.d.) using a catalyst weight of 2 g. All other features of the system were identical to that described previously.¹³

Isobutane, supplied by two coupled high-pressure syringe pumps, was used to fill the reactor system at the desired pressure at startup. For the alkylation reaction step, a separate high-pressure syringe pump was employed to supply the reaction feed mixture for the reaction phase. Isobutane and *trans*-2-butene were premixed in a high-pressure vessel to obtain the desired isoparaffin-to-olefin molar ratio (iP/O). For the regeneration step, the high-pressure syringe pumps that were used to supply isobutane for system startup were used to supply isobutane to the reactor system.

Gas chromatographic (GC) analyses of the reactor effluent were performed on-line using a Hewlett-Packard 5890 Series II gas chromatograph (Wilmington, DE) equipped with an automated, high-pressure sample valve, electronic pressure controller, and flame ionization detector (FID) as previously described.¹³

3. Experimental Studies. Experiments were performed to assess the efficacy of the supercritical isobutane regeneration process for partially deactivated USY catalyst. Previous testing utilizing this regeneration process achieved a maximum of 82% recovery of trimethylpentane (TMP) production in single regenerations if the catalyst was fully deactivated,^{13,14} which we had defined as the cessation of TMP production. On the basis of our postulated process for the regeneration,^{13,15} we surmised that a higher and perhaps sustained recovery of catalyst activity could be achieved if the catalyst were

Table 1. Reaction and Regeneration Methods and Regeneration Criteria Utilized to Regenerate Partially Deactivated USY Catalyst^a

step	criterion A	criterion B
first alkylation reaction step	proceed until butene conversion drops to 95%	180 min reaction duration
regeneration step		
flush system with isobutane at 60 °C	10 min	10 min
increase reactor temp to 180 °C	30 min	30 min
supercritical regeneration	120 min	120 min
decrease reactor temp to 60 °C	30 min	30 min
second alkylation reaction step	proceed until butene conversion drops to 95%	180 min reaction duration

^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. The recycle ratio employed in all tests was 25:1.

regenerated with supercritical isobutane prior to the formation of dehydrogenated, condensed carbonaceous species within the catalyst.

Initial single regeneration experiments used a USY catalyst partially deactivated in a controlled manner. To control the amount of deactivation, two independent criteria were defined to determine the point at which to stop the alkylation reaction and begin the in situ regeneration step. The first criterion, criterion A, was defined as the point at which the *trans*-2-butene (T2B) fractional conversion declined to 95%. After the regeneration, the second reaction step was begun and allowed to proceed until the T2B fractional conversion once again decreased to 95%, and the % recovery of activity was calculated by ratio. Because of cumulative effects of apparently unremovable fouling compounds,¹⁵ the use of criterion A to define the end of the reaction step generally resulted in a second reaction step that was shorter in duration than the first. A second criterion that would be more amenable to industrial application was defined that allowed a constant reaction time for each reaction step. On the basis of the experimentally observed, time-dependent butane conversion and product yields, criterion B was defined as a constant 3 h of reaction time for both reaction steps. As with the other criterion, the second reaction step (after the regeneration) was allowed to proceed for an identical time period (3 h), and the % recovery of activity was calculated by ratio. Multiple regeneration tests were then conducted using each criterion and the activity recoveries and product compositions were compared.

4. Experimental Methods. 4.1. Alkylation Reaction. Alkylation was conducted in the reactor using 2 g of catalyst packed into a section of high-pressure stainless steel tubing 1.27 cm (1/2 in.) in diameter. The catalyst was held in place by plugs of quartz wool at each end of the catalyst bed. It was previously demonstrated that, under typical system conditions, the alkylation reaction was free from external mass-transfer effects.⁶ All alkylation reactions were performed at 60 °C and 111 bar (1600 psig), at an olefin weight hour space velocity (OWHSV) of 0.2 and an isoparaffin/olefin ratio (iP/O) of 20:1. An iP/O ratio of 20:1 was chosen since a preliminary assessment by the project team found that this would be acceptable under certain economic assumptions. Single regeneration experiments were run as follows. The reactor system was initially filled throughout with isobutane at the desired reaction temperature and pressure. At time zero, the flow of the reaction mixture (isobutane + *trans*-2-butene) to the system was started at 0.242 mL/min. Since the residence time of the reaction system was 20–30 min at this flow rate, products were not initially observed until ~20 min into the experiment. The reaction was allowed to proceed until criterion A or B was reached, signaling

a requirement to switch to the regeneration step, at which time the flow of the reaction mixture was stopped and the regeneration procedure was begun. Regeneration criteria A and B are shown in Table 1, together with the reaction and regeneration steps.

4.2. Regeneration Method. Regeneration of the partially deactivated catalyst bed was conducted as previously described using isobutane¹⁴ and is outlined in Table 1. After stopping the reaction mixture flow, isobutane at 111 bar was pumped through the reactor at an isobutane weight hour space velocity (IWHSV) of 33 (g of isobutane)/(g of catalyst)/h throughout the entire regeneration process. The reactor temperature was initially held at 60 °C for 10 min to wash the reaction products from the catalyst bed. The reactor temperature was then increased to 180 °C at a rate sufficient to attain the temperature change in 30 min. Isobutane continued to flow through the reactor at 180 °C for a supercritical regeneration period of 120 min. After the regeneration step was completed, the temperature was decreased to 60 °C in preparation for the second alkylation step, at a rate sufficient to reach 60 °C in 30 min. After the system temperature was stable, the isobutane flow was stopped and the flow of the reaction mixture was restarted at alkylation conditions.

4.3. Data Analysis. Yields of products from the alkylation reaction were calculated by integrating production rate versus time for each reaction cycle. The production rates (g/h) were calculated from the feed input rate (g/h) and the product weight fraction (wt %) and plotted versus time. The integrals were normalized by dividing by the total weight of catalyst in each respective 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%.

Results

1. Single Regeneration, 95% Conversion of T2B (Criterion A). The time course of the fractional conversion of T2B for a single regeneration of partially deactivated USY using criterion A is shown in Figure 2. Also included in Figure 2 are the time courses of the C₅₊ and trimethylpentane (TMP) product yields, as weight percentages of T2B in the feed. The first reaction step proceeded 6.17 h before the T2B conversion decreased to 95%, at which point the reactant flow was stopped. The catalyst was then regenerated in situ with supercritical isobutane. After regeneration, the alkylation reaction was restarted and concluded when the T2B conversion decreased to 95%, which occurred after a second reaction time of 5.55 h. Thus, using criterion A resulted in a 10% decrease in the reaction duration. The time courses of the TMP yields for the two reaction steps

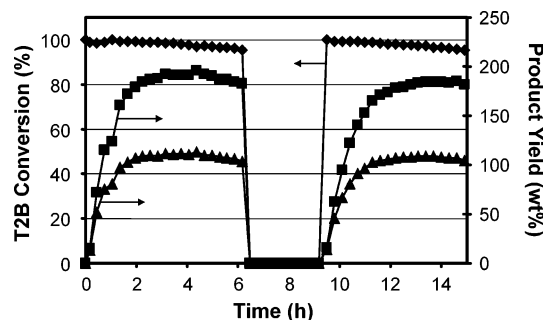


Figure 2. Fractional *trans*-2-butene (T2B) conversion (◆), and C_{5+} (■) and TMP (▲) product yields (as wt % of T2B in feed) for a single regeneration of partially deactivated and reactivated USY catalyst using regeneration criterion A. Reaction conditions were: $T = 60\text{ }^{\circ}\text{C}$; $P = 111\text{ bar}$; $iP/O = 20:1$; $OWHSV = 0.2$; and volumetric recycle ratio = 25:1. Regeneration conditions were: $T = 180\text{ }^{\circ}\text{C}$; $P = 111\text{ bar}$; time at conditions = 2 h; isobutane flow = 33 g/(g of catalyst)/h.

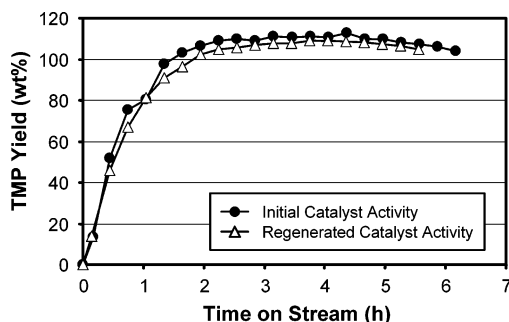


Figure 3. TMP product yield (as % of T2B in feed) for the initial and regenerated USY catalyst regenerated and shown in Figure 2, plotted on an individual reaction time-on-stream time scale for direct comparison of the time courses.

are plotted on an individual reaction time-on-stream scale in Figure 3. In Figure 3, the reaction time of zero is the beginning of each reaction step coinciding with the start of the flow of the reaction mixture, either for the initial reaction step or after the regeneration step. The time-integrated product yields in the first reactor step were 1.92 and 1.13 g of C_{5+} and TMP per gram of catalyst, respectively. The integrated product yields in the second reactor step were 1.60 and 0.98 g of C_{5+} and TMP per gram of catalyst, respectively. The unrecovered activity losses combined with the decreased reaction time-on-stream resulted in 83.4% and 86.4% recovery of the fresh catalyst C_{5+} and TMP activities, respectively. This experiment was independently repeated in a second reactor system and achieved 79.7% and 81.0% recovery of the fresh catalyst C_{5+} and TMP activities, respectively. Thus, the regeneration effectiveness of the partially deactivated USY catalyst using criterion A was comparable to the observed maximum 82% regeneration of the TMP activity of a completely deactivated catalyst.¹⁴

2. Single Regeneration, 3 h Reaction Time (Criterion B). The time course of the fractional conversion of T2B for a single regeneration of partially deactivated USY using criterion B is shown in Figure 4. Also included in Figure 4 are the time courses of the C_{5+} and TMP product yields, as weight percentages of T2B in the feed. The first reaction step proceeded the prescribed 3.00 h, at which point the T2B conversion was 98.1%, the reactant flow was stopped, and the catalyst was regenerated. After regeneration, the alkylation reaction was restarted and concluded after 2.98 h for a total reaction time of 5.98 h, at which point the T2B conver-

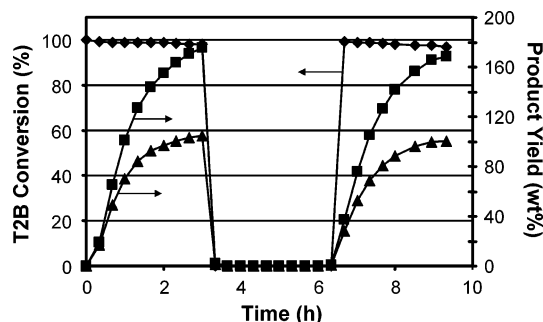


Figure 4. Fractional *trans*-2-butene (T2B) conversion (◆), and C_{5+} (■) and TMP (▲) product yields (as % of T2B in feed) for a single regeneration of partially deactivated and reactivated USY catalyst using regeneration criterion B. Reaction conditions were: $T = 60\text{ }^{\circ}\text{C}$; $P = 111\text{ bar}$; $iP/O = 20:1$; $OWHSV = 0.2$; and volumetric recycle ratio = 25:1. Regeneration conditions were: $T = 180\text{ }^{\circ}\text{C}$; $P = 111\text{ bar}$; time at conditions = 2 h; isobutane flow = 33 g/(g of catalyst)/h.

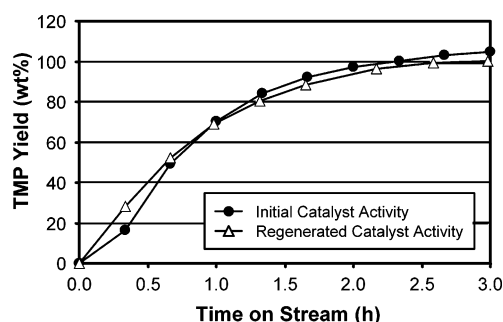


Figure 5. TMP product yield (as % of T2B in feed) for the initial and regenerated USY catalyst regenerated and shown in Figure 4, plotted on an individual reaction time-on-stream time scale for direct comparison of the time courses.

sion was 96.8%. Use of criterion B resulted in a 1.3% decrease in the T2B conversion after a single regeneration. The time courses of the TMP yields for the two reaction steps are plotted on an individual reaction time-on-stream scale in Figure 5. Similar to Figure 3, time zero indicates the beginning of each reaction step coinciding with the start of the flow of the reaction mixture, either for the initial reaction step or after the regeneration step. The time-integrated product yields in the first reactor step were 0.692 and 0.446 g of C_{5+} and TMP per gram of catalyst, respectively. The integrated product yields in the second reactor step were 0.715 and 0.453 g of C_{5+} and TMP per gram of catalyst, respectively. Thus, using criterion B resulted in 103.3% and 101.5% recovery of the fresh catalyst C_{5+} and TMP activities, respectively. This experiment was independently repeated in a second reactor system and achieved 110.6% and 110.7% recovery of the fresh catalyst C_{5+} and TMP activities, respectively. Hence, regeneration of the partially deactivated USY catalyst using criterion B was superior in effectiveness to using criterion A and to the regeneration of a completely deactivated catalyst.¹⁴

3. Multiple Regeneration, 95% Conversion of T2B (Criterion A). Multiple regeneration testing was conducted using criterion A in order to assess the expected maximum number of reaction steps the catalyst could perform or the maximum number of steps until a more stringent regeneration method to remove the recalcitrant fouling compounds, such as oxidative regeneration, would be required. Nine reaction steps were performed (eight regenerations) in sequence, with the test being stopped because of a significant, cumula-

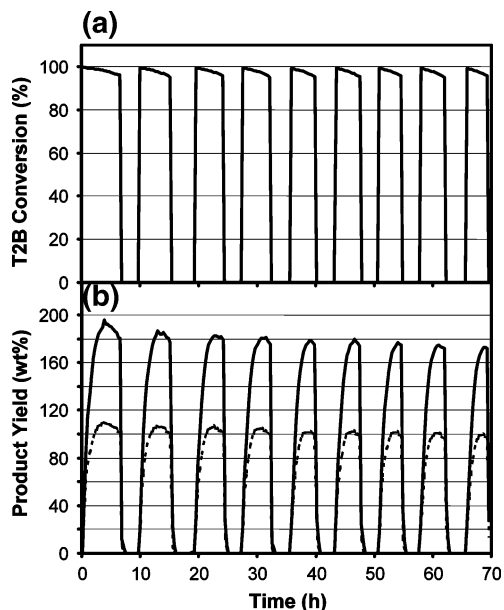


Figure 6. Time courses of fractional T2B conversion and C_{5+} and TMP product yields for 9 consecutive reaction steps (8 regenerations) using criterion A to determine the start times for the regeneration steps. Top panel = T2B conversion and bottom panel = C_{5+} and TMP product yields presented as a weight percentage of T2B in the feed. The solid line is the C_{5+} yield, and the dashed line is the TMP yield.

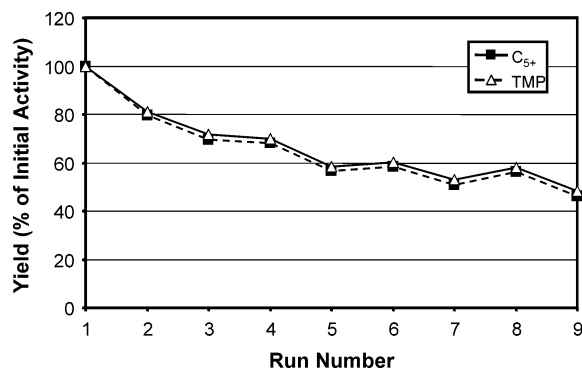


Figure 7. Variation of the time-integrated product yield, presented as a percent of that observed in the initial run (fresh catalyst), with consecutive reaction steps using criterion A to determine regeneration start times.

tive loss of catalyst activity. The time courses of T2B conversion and C_{5+} and TMP product yields are shown in Figure 6. As observed in the single regeneration using criterion A, some of the lost activity was not recoverable via regeneration of the catalyst using supercritical isobutane. This is most noticeable in the cumulatively greater losses in C_{5+} and TMP product yields for each successive reaction step (Figure 6b) and is also evidenced in Figure 6a by the increasingly negative slope of the T2B fractional conversion with time for each successive reaction step. The maximum observed product yield of C_{5+} (as wt % of T2B in the feed) decreased ~12% from 196 wt % in the initial reaction step to 173 wt % in the ninth reaction step. Similarly, the maximum observed TMP conversion dropped by 9.5%, from 110 to 99 wt %. The time-integrated product yields, shown in Figure 7 as a percentage of fresh catalyst (initial) yield, reveal the lost activity with each consecutive reaction step. The greatest loss in integrated yield was due to the reduced time required to reach 95% conversion of T2B. By the end of the test, the time required to reach 95% conversion had decreased from an initial time

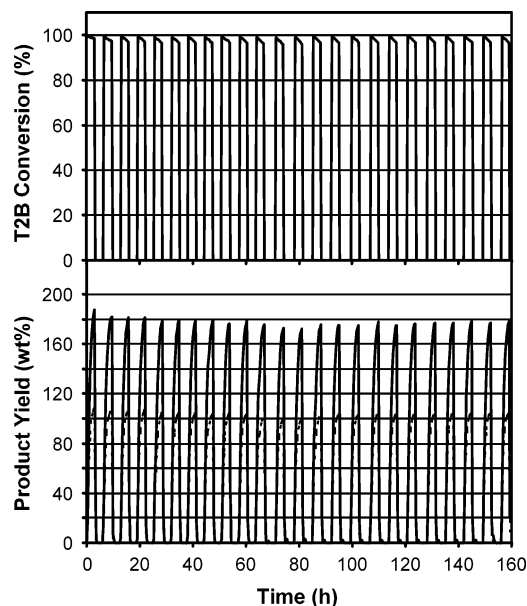


Figure 8. Time courses of fractional T2B conversion and C_{5+} and TMP product yields for 24 consecutive reaction steps (23 regenerations) using criterion B to determine the start times for the regeneration steps. Top panel = T2B conversion and bottom panel = C_{5+} and TMP product yields presented as a weight percentage of T2B in the feed. The solid line is the C_{5+} yield, and the dashed line is the TMP yield.

of 6.55 h to 3.67 h after eight regeneration steps, a 44% decrease in reaction time-on-stream. The final reaction step (run 9, Figure 7) yielded 46.1% and 48.2% of the fresh catalyst C_{5+} and TMP products, respectively. The C_{5+} and TMP yields after nine reaction steps in an independent replicate conducted in a second reactor system were 41.4% and 44.4% of the fresh catalyst C_{5+} and TMP activities, respectively.

4. Multiple Regeneration, 3 h Reaction Time (Criterion B). Multiple regeneration testing was next conducted using criterion B as the criterion for stopping the reaction step and initiating the regeneration step. This test was much more effective, resulting in 24 reaction steps (23 regenerations) in sequence, although the test was stopped because of time constraints rather than because of cumulative loss of catalyst activity. It is unknown how many additional reaction steps could have been performed before the catalyst would have been unusable or would have required a more stringent regeneration method. The time courses of T2B conversion and C_{5+} and TMP product yields are shown in Figure 8, and the integrated product yields are shown in Figure 9. Catalyst activity for both C_{5+} and TMP increased ~11% from the first to the second reaction step, with yields increasing from 0.738 and 0.459 g/(g of catalyst) to 0.816 and 0.508 g/(g of catalyst), respectively. The final reaction step (run 24, Figure 9) yielded 101.7% and 103.7% of the fresh catalyst C_{5+} and TMP products, respectively. The C_{5+} and TMP yields after 23 reaction steps in an independent replicate conducted in a second reactor system were 84.0% and 78.3% of the fresh catalyst C_{5+} and TMP activities, respectively, which were significantly different from those observed in the first experiment. This was the result of an operational difficulty encountered while manually adjusting the reaction and regeneration conditions in the second experiment, which allowed more extensive deactivation of the catalyst before the regeneration cycle was started. In an earlier study, we demonstrated that

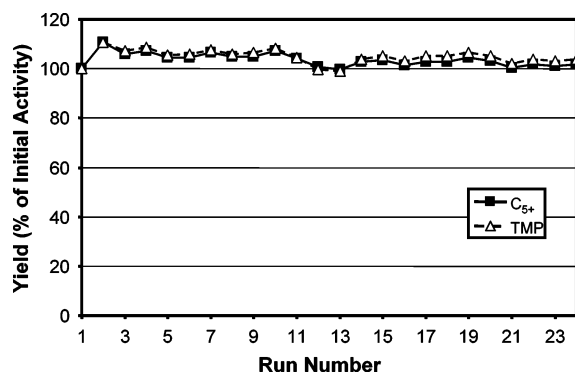


Figure 9. Variation of the time-integrated product yield, presented as a percent of that observed in the initial run (fresh catalyst), with consecutive reaction steps using criterion B to determine regeneration start times.

the regeneration process was most effective in recovering catalyst surface area and micropore volume from samples regenerated after a short TOS, when the level of activity for TMP production was high.¹⁵ In that study, samples that were allowed to react for a longer TOS contained unsaturated hydrocarbons that, instead of being extracted by the supercritical fluid, dehydrogenated during the SFR process to produce more condensed species. The two experiments were consistent up to the point of the process upset, which occurred around runs 8–10, at which point the C₅₊ and TMP yields were 105.0% and 105.8% in the first experiment and 102.0% and 100.3% in the second experiment, respectively. Hence, the significantly lower yields in the second experiment tend to support our prior observations.¹⁵ In any event, even at the average of ~90% activity remaining after 24 reaction steps, which equates to 72 h of cumulative time-on-stream, this is a very significant improvement over the 5–6 h of activity obtained using this catalyst without supercritical isobutane regeneration.

As with the use of criterion A, the use of criterion B to determine regeneration start times resulted in a time-dependent decline in the maximum product yield (Figure 8), although it happened much more slowly and to a lesser degree than that observed with criterion A. As detailed in Table 2, the maximum observed product yield of C₅₊ (as wt % of T2B in the feed) decreased 4.3% from 187 wt % in the initial reaction step to 179 wt % in the 24th reaction step. This is a 0.20% decrease in alkylate yield per reaction step using criterion B, as compared to a 1.5% decrease per reaction step using criterion A. Similarly, the maximum observed TMP yield dropped by 4.6%, from 108 wt % to 103 wt %, which is a 0.23% decrease per reaction step for criterion B versus a 1.2% decrease per reaction step for criterion A. Hence, with criterion B, there was still some (smaller) level of unrecoverable catalyst activity, indicating that there is a limit to the number of times the catalyst can be regenerated using supercritical isobutane. The tests described here, however, indicate that by regenerating partially deactivated catalyst, the catalyst lifetimes achievable using a USY catalyst to perform alkylation reactions can be increased by several orders of magnitude by using supercritical isobutane regeneration.

The maximum instantaneous product yields for C₅–C₉₊ alkylation products are shown in Table 2 for each of the 24 sequential reaction steps run using criterion B to determine start times for the regeneration steps (the C₅₊ and TMP data are plotted in Figure 9). As noted

Table 2. Instantaneous Yields of C₅–C₉₊ Alkylation Products for 24 Sequential Reaction Steps Using Criterion B

reaction step no.	instantaneous product yields (g/(100 g of butene))								
	C ₅₊	C ₅	C ₆	C ₇	C ₈	TMP	DMH	other C ₈	C ₉₊
1	187	16	11	15	140	108	29	2.5	5.6
2	182	15	11	14	135	106	27	2.9	6.5
3	181	15	11	14	134	105	26	3.5	7.7
4	181	15	11	15	134	105	25	3.6	7.8
5	178	15	10	14	131	103	24	3.6	8.5
6	179	15	10	14	130	103	24	3.7	10
7	178	15	10	14	130	103	24	3.7	9.1
8	179	15	11	14	129	102	24	3.7	10
9	176	15	10	14	130	103	24	3.3	7.9
10	179	15	10	14	129	102	24	4.0	10
11	176	15	10	14	128	100	24	3.9	9.1
12	173	15	10	14	124	98	23	3.7	11
13	172	15	10	14	124	98	23	3.8	10
14	175	15	10	14	128	101	24	4.0	7.8
15	175	15	10	14	129	102	24	3.7	8.3
16	175	15	10	13	128	101	23	3.7	9.3
17	178	15	10	14	131	102	24	4.8	10
18	175	14	12	14	132	102	25	4.9	5.8
19	176	15	10	14	129	102	24	3.8	8.4
20	177	15	10	14	129	102	24	3.8	8.9
21	177	14	11	14	133	103	24	6.6	5.1
22	178	14	11	14	133	103	24	6.8	6.1
23	177	14	10	14	133	103	24	6.2	5.9
24	179	14	10	14	133	103	24	7.3	7.3
avg	178	15	11	14	131	103	24	4.2	8.1
stdev	3.2	0.45	0.37	0.30	3.4	2.3	1.3	1.2	1.6
stdev (%)	1.8	3.0	3.5	2.1	2.6	2.2	5.2	29	20

above, there was a slow decline in alkylate and TMP yields over the 24 reaction steps, with drops in C₅₊ and TMP yields amounting to 0.20% and 0.23% per reaction step. The overall decline in C₅₊ yield (24th step versus 1st step shown in Table 2) was 4.3%, comprised of 12%, 10%, 4.2%, and 4.6% declines in the yields of C₅, C₆, C₇, and C₈, respectively, based on the absolute change relative to the initial values. The 4.2% decline in C₈ production comprised a 4.6% decline in TMP production [108 to 103 (g of TMP)/100 (g of butene)], a 17% decline in DMH production [29 to 24 (g of DMH)/(100 g of butene)], and a 187% increase in other C₈s [2.5 to 7.3 (g of other C₈s)/100 (g of butene)] over the 24 sequential reaction steps. Note that the low amounts of other C₈s in the alkylate rendered the increases to be of little significance in terms of the overall alkylate composition. Finally, the production of C₉₊ increased by 30% from 5.6 to 7.3 (g of C₉₊)/100 (g of butene). The largest declines occurred when going from the 1st reaction step to the 2nd. Overall, the instantaneous yields were stable over the 24 reaction steps, with low standard deviations in yields over the 24 reaction steps. This was true for all but other C₈s and C₉₊, which together comprised only 8.1 and 14.6 g/100 (g of butene) in the 1st and 24th reaction steps, respectively.

The overall product quality, defined here as the time-integrated fractional composition of the liquid alkylate product, is presented for C₅–C₉₊ products in Table 3. The fresh catalyst (1st reaction step) produced alkylate that comprised 19.7 wt % C₅–C₇, 76.9 wt % C₈, and 3.4 wt % C₉₊. The fresh catalyst alkylate contained 59.8 wt % TMP and 15.6 wt % dimethylhexane (DMH) on a total weight basis, with a TMP/DMH ratio of 3.84. The 24th reaction step produced alkylate that comprised 18.5 wt % C₅–C₇, 78.3 wt % C₈, and 3.2 wt % C₉₊, containing 61.7 wt % TMP and 12.4 wt % DMH on a total weight basis, with a TMP/DMH ratio of 4.97. Thus, the product composition on a total alkylate weight basis was quite stable, with a trend toward higher TMP/DMH ratios.

Table 3. Overall Product Quality for 24 Sequential Reaction Steps Using Criterion B

reaction step no.	% of total alkylate									TMP/DMH
	C ₅	C ₆	C ₇	C ₈	TMP	DMH	other C ₈	C ₉₊		
1	7.6	5.1	7.1	76.9	59.8	15.6	1.5	3.4	3.84	
2	7.5	5.0	7.1	77.0	61.2	14.0	1.8	3.5	4.37	
3	6.9	5.3	7.2	76.2	61.2	13.6	1.4	4.4	4.52	
4	6.8	4.8	7.3	77.1	61.6	13.7	1.8	4.1	4.51	
5	7.4	4.8	7.4	75.5	60.9	12.7	1.8	4.9	4.78	
6	7.5	4.7	7.3	75.5	60.9	12.8	1.9	4.9	4.78	
7	7.5	4.7	7.3	75.4	61.1	12.3	1.9	5.1	4.95	
8	7.4	4.8	7.5	75.1	60.9	12.3	1.9	5.2	4.97	
9	7.7	4.7	7.3	76.0	61.1	12.9	2.0	4.3	4.73	
10	7.8	4.7	7.4	75.2	60.9	12.4	1.9	4.9	4.93	
11	7.6	4.9	7.6	74.5	60.0	12.4	2.1	5.5	4.85	
12	8.0	4.9	7.7	73.8	59.4	12.1	2.2	5.7	4.89	
13	7.9	4.8	7.6	74.1	59.8	12.1	2.2	5.7	4.95	
14	7.1	4.7	6.9	76.7	61.1	12.6	3.1	4.6	4.87	
15	7.0	4.9	6.8	76.8	61.3	12.5	3.0	4.5	4.88	
16	7.4	4.6	7.4	75.1	60.9	12.2	2.0	5.5	5.01	
17	7.3	4.7	7.5	76.1	61.7	12.3	2.1	4.5	5.00	
18	6.8	6.0	5.9	78.6	61.9	13.9	2.8	2.8	4.45	
19	7.3	4.6	7.3	75.2	60.9	12.2	2.1	5.5	5.01	
20	6.9	5.2	7.3	75.6	61.3	12.3	2.0	5.0	4.97	
21	6.8	4.8	7.5	78.5	61.3	13.0	4.3	2.4	4.73	
22	6.7	4.8	7.3	78.6	61.7	12.4	4.4	2.6	4.97	
23	12.3	4.5	6.6	74.0	58.2	11.7	4.2	2.6	4.98	
24	6.8	4.7	7.1	78.3	61.7	12.4	4.2	3.2	4.97	
avg	7.5	4.8	7.2	76.1	60.9	12.8	2.4	4.4	4.79	
stdev	1.1	0.3	0.4	1.4	0.9	0.8	0.9	1.1	0.28	
stdev (%)	14.6	6.2	5.3	1.9	1.4	6.6	37.7	24.4	5.8	

TMP overall product compositions, based on time-integrated yields, are presented in Table 4 for the 24 reaction steps, on both total alkylate and total TMP bases. Note that our GC method was unable to completely separate 2,5-DMH and 2,2,3-TMP. Since this combined peak was typically small compared to the total measured TMPs (2.0% – 4.6%), we lumped these two compounds under the label 2,5-DMH and included it in the DMH totals: this provided the most conservative estimate of total TMP production and the TMP/DMH ratio. On a total alkylate basis, the fresh catalyst alkylate contained 28.4 wt % 2,2,4-TMP, 12.1 wt % 2,3,4-TMP, and 19.3 wt % 2,3,3-TMP. This amounted to 47.5%, 20.2%, and 32.2% of these products on a total TMP basis, respectively. The alkylate produced in the 24th reaction step contained 21.0 wt % 2,2,4-TMP, 16.7 wt % 2,3,4-TMP, and 23.9 wt % 2,3,3-TMP, amounting to 34.1%, 27.1%, and 38.8% of these products on a total TMP basis, respectively. This indicates a 28% decrease in the relative amount of 2,2,4-TMP produced, and increases of 34% and 20% in the relative amounts of 2,3,4-TMP and 2,3,3-TMP produced, respectively.

Discussion

Catalysts that were partially deactivated appeared to regenerate better than the completely deactivated catalysts reported previously.^{13,14} For single and multiple regenerations, stopping the reaction at a fixed TOS of 3.0 h produced superior results compared to allowing the butene conversion activity to decline to 95%, which initially occurred at about 6 h TOS. Utilization of the criteria of butene conversion declining to 95% to halt the reaction and initiate regeneration resulted in shorter TOSs for all subsequent reaction steps.

Higher supercritical isobutane regeneration effectiveness at either shorter times-on-stream or lower levels of deactivation is a reasonably anticipated result. 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 a higher OWSHV was employed. Catalyst samples were subjected to four levels of deactivation and either removed for examination or subjected to supercritical isobutane regeneration and then removed and examined. The four levels of deactivation that the catalyst samples were exposed to included: within the useful catalyst lifetime (at 100% butene conversion), toward the end of the useful catalyst lifetime (after butene breakthrough), in the rapid deactivation stage, and at the last stage of deactivation.

In that prior work,¹⁵ it was found that as reaction TOS increased, the catalyst surface area and micropore volume decreased due to the adsorption of hydrocarbons mainly in the supercages of the zeolite structure. The molecular weight of the hydrocarbon species, which were mostly highly branched paraffins, increased with TOS, and at longer TOS, unsaturated cyclic structures were detected by UV-vis on the catalyst surface. The supercritical regeneration process was effective in restoring surface area and micropore volume. It extracted most coke precursors from samples exposed to a short TOS. Samples that were allowed to react for a 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 our current study, the use of either criteria terminated the reaction step within the useful catalyst lifetime, as defined by Sherwood.¹⁶ However, our prior work¹⁵ has shown that, even within the useful catalyst lifetime, as TOS increased, a higher quantity of coke adsorbed, resulting in reduced surface area and micropore volume and changes in the coke precursor structure. For this work, at the higher TOS, it could be expected that higher levels of adsorbed hydrocarbons would result in lower catalyst surface area and micropore volume. Further, the hydrocarbon species should have higher molecular weights and be more dehydrogenated. These species would be more difficult to extract, leading to lower levels of activity recovery.

Several interesting results were observed when the reaction was stopped at a fixed time-on-stream of 3.0 h. Integrated product yields were higher compared to those obtained from the fresh catalyst, maximum product yields declined only slightly per run (0.20% or 0.23% for C₅₊ and TMP, respectively), and overall product quality improved. Over 24 reaction steps, the TMP selectivity was relatively stable while DMH selectivity decreased 3.2 wt %, providing an improvement in the TMP/DMH ratio from ~3.8 to ~5.0. Further, a clear shift was observed in the TMP composition.

The relative stability in activity per reaction/regeneration step was due to both the high levels of hydrocarbon removal, as previously reported,¹⁵ and the minimum damage caused to the catalyst due to mild regeneration conditions as compared to oxidation or hydrogenation. The higher activity of the regenerated catalyst compared to the fresh catalyst was consistently observed for catalyst reactivated after 3 h of alkylation reaction. This higher activity was the result of higher product yields in the first hour of reaction, as seen most clearly in Figure 5. We attribute this higher first-hour yield to the presence of *tert*-butyl carbenium ions on the catalyst surface after the regeneration process, which reduced the time necessary to initiate the alkylation

Table 4. Overall Trimethylpentane Compositions for 24 Sequential Reaction Steps Using Criterion B

reaction step no.	% of total alkylate			% of TMPs		
	2,2,4-TMP	2,3,4-TMP	2,3,3-TMP	2,2,4-TMP	2,3,4-TMP	2,3,3-TMP
1	28.4	12.1	19.3	47.5	20.2	32.2
2	25.7	14.1	21.4	42.0	23.0	35.0
3	23.8	15.0	22.5	38.8	24.5	36.7
4	23.3	15.5	22.8	37.9	25.2	37.0
5	22.5	15.6	22.8	37.0	25.7	37.4
6	22.1	15.9	23.0	36.3	26.0	37.7
7	21.9	16.1	23.1	35.9	26.3	37.8
8	21.7	16.1	23.1	35.7	26.5	37.8
9	22.2	16.0	22.9	36.3	26.2	37.5
10	21.8	16.1	23.0	35.8	26.4	37.8
11	21.6	15.8	22.6	36.0	26.3	37.7
12	20.4	16.2	22.7	34.4	27.3	38.3
13	20.3	16.5	23.0	33.9	27.6	38.5
14	20.8	16.7	23.5	34.1	27.4	38.5
15	21.0	16.7	23.6	34.3	27.2	38.5
16	20.9	16.6	23.4	34.3	27.3	38.4
17	21.3	16.8	23.6	34.6	27.2	38.2
18	21.1	16.7	24.1	34.1	27.0	38.9
19	20.9	16.7	23.4	34.2	27.4	38.4
20	21.3	16.6	23.4	34.8	27.1	38.1
21	21.3	16.4	23.7	34.7	26.7	38.6
22	20.9	16.8	24.1	33.8	27.2	39.1
23	19.6	15.9	22.6	33.8	27.3	38.9
24	21.0	16.7	23.9	34.1	27.1	38.8
avg	21.9	16.0	23.0	36.0	26.3	37.7
stdev	1.9	1.0	1.0	3.1	1.7	1.5
stdev (%)	8.5	6.6	4.3	8.6	6.4	3.9

reaction. In our prior work examining light hydrocarbons for the activity recovery of a USY alkylation catalyst, we found that the highest regeneration effectiveness occurred when the reactivation fluid contained a tertiary carbon.¹³ The data from that work suggested that the supercritical regeneration process was reactive. Supercritical isobutane facilitates a hydride transfer reaction step to release an adsorbed high-molecular-weight carbenium ion from the catalyst surface.¹³ In the process, a *tert*-butyl carbenium ion is adsorbed to the catalyst surface and is then available for reaction when the regeneration is completed and the alkylation is reinitiated.

The change observed in product selectivity after 24 reaction steps suggests an adjustment in the catalytic functionality following the supercritical fluid regeneration steps. Solid alkylation catalysts are known to catalyze not only the alkylation reaction but also isomerization, cracking, and polymerization reactions.⁴ After 24 reaction steps, the TMP/DMH ratio was observed to improve. Several different mechanisms could account for the variation in the TMP and DMH composition. In the alkylation initiation reaction, butene reacts to form a *sec*-butyl carbenium ion, which reacts with isobutane through a hydride transfer step to form a more stable *tert*-butyl carbenium ion.^{17,18} In subsequent reaction steps with 2-butene, TMP products are produced. However, the *sec*-butyl carbenium ion may instead react directly with 2-butene to form 3,4-dimethylhexane cations that may undergo various hydride or methyl shifts leading to the production of DMH isomers.^{17,18} If the supercritical isobutane regeneration process results in the generation of adsorbed *tert*-butyl carbenium ions prior to the start of the subsequent alkylation reaction cycle, then the ratio of *tert*-butyl to *sec*-butyl carbenium ions would increase, yielding an improvement in the TMP-to-DMH selectivity. Another possible explanation of the shift could be due to changes in isomerization rates. TMPs are the primary product of the alkylation of 2-butene and isobutane. DMHs can

be formed from the isomerization of 2-butene to 1-butene followed by alkylation with isobutane.^{4,19} Thus, the decrease in DMH selectivity may suggest an advantageous loss of butene isomerization activity. Additional mechanisms could also be at play.⁴ Although the data in this work cannot identify the responsible mechanism, the former explanation is consistent with the higher integrated product yields observed following supercritical isobutane regeneration.

The shift in TMP isomer distribution also reveals another shift in catalyst behavior. Variations in TMP isomer selectivity have been attributed to the effect of pore size on the formation of transition-state intermediates and relative product diffusion rates.^{4,18} Initially, our catalyst favored selectivity to the bulkier 2,2,4-TMP over either one of the other smaller isomers. As the number of reaction steps increased, 2,2,4-TMP isomer selectivity decreased 13.4 wt % while 2,3,4-TMP and 2,3,3-TMP selectivity increased 6.9 wt % and 6.6 wt %, respectively. The largest changes in isomer selectivity were observed between the first and second reaction step. This trend suggests that pore diameter may be decreasing because of the buildup of nonextractable hydrocarbon species resulting in a restriction in the formation of the bulkier transition-state intermediates and restricted product diffusion.

The purpose of this effort was to explore the effectiveness of supercritical isobutane for multiple regenerations of a solid acid catalyst used in isobutane/butane alkylation. This effort was constrained to that purpose, and the exploration of catalysts, reaction conditions, and regeneration conditions was not conducted here. Although the effect of regeneration conditions was not explored in this study, our previous efforts explored regeneration conditions extensively.¹⁴ That work found that regeneration effectiveness was not significantly influenced by pressure between 42 and 139 bar, thus, lower pressures that offer lower capital and operating costs may be possible. Alkylate yield and quality, which were only moderately affected by regeneration condi-

tions as discussed above, are less than industrially desired. These factors are primarily a function of catalyst properties. Thus, additional efforts to develop improved solid alkylation catalysts are still necessary.

Conclusions

Supercritical isobutane regeneration appears to be a promising technique for enhancing solid-catalyzed isobutane/butene alkylation. By limiting the level of deactivation prior to regeneration, high levels of catalyst activity recovery may be achieved. For single and multiple regenerations, stopping the reaction at a fixed TOS of 3.0 h produced superior results compared to allowing butene conversion activity to decline to 95%. Twenty-four reaction steps were performed, resulting in a minor activity loss per step and improved product quality. Additional work in catalyst development and reactor design will still be required before the liquid acid processes can be replaced by solid catalysts.

Acknowledgment

The authors kindly acknowledge in-kind financial contributions to this work by Marathon Ashland Petroleum, LLC, through a Cooperative Research and Development Agreement. This work was supported by the U.S. Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory, under contract number DE-AC07-99ID13727.

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Received for review February 14, 2005

Revised manuscript received April 20, 2005

Accepted May 3, 2005

IE050176F