INCREASING MTBE PRODUCTIVITY WITHOUT INCREASING CAPITAL COSTS

Richard Chavez
Lyondell Petrochemical Company

Dr. Robert Olsen
Rohm and Haas Company

Dr. Michael Ladisch
Purdue University

Introduction
As a result of the motor vehicle emissions standards imposed by the Clean Air Act Amendments of 1990, there is a potential for a large increase in demand for oxygenates such as MTBE. According to the Oxygenated Fuels Association's Report, "Benefits of a National Oxygenated Fuels Policy," oxygenates are now added to more than 30% of the U.S. gasoline pool, which represents about 4% of the total amount of gasoline consumed. By the year 2000, oxygenates are expected to be added to 70% of the U.S. gasoline pool, and will represent nearly 10% of the total amount of gasoline consumed.

With increasing demand for MTBE, there is interest in finding a cost effective way to increase production from existing process units. One way is to use a catalyst with increased activity. Rohm and Haas has developed Amberlyst® 35 Wet polymeric catalyst as its "next generation" catalyst for enhancing oxygenate production.

Development Experience
Rohm and Haas has a long history in the polymeric catalyst market. Amberlyst® 15 Wet was the original catalyst used in MTBE production. The preferred commercial MTBE catalyst for nearly two decades has been a polymeric catalyst composed of sulfonic acid chemically bound to a cross-linked copolymer of styrene and divinylbenzene. The desirable performance of the catalyst includes moderate activity coupled with fairly high isobutylene conversion and minimal by-product formation. There has been commercial interest in an MTBE catalyst with higher activity, which would increase isobutylene conversion without increasing by-product formation.

The activity coefficients for methanol, isobutylene, and MTBE, together with the equilibrium constant, determine the equilibrium conversion that is possible. The activity coefficients of at least one of the three reaction components for Amberlyst 35 Wet differ significantly from Amberlyst 15 Wet. As a result, Amberlyst 35 Wet affects a higher equilibrium conversion relative to Amberlyst 15 Wet for the MTBE reaction. It is hypothesized that this difference in activity coefficients between polymeric catalysts is due to a considerable difference in the properties of their respective gel phases.

Pilot reactors and differential reactors have been used to study the performance of Amberlyst 35 Wet versus Amberlyst 15 Wet. Higher isobutylene (IB) conversions for Amberlyst 35 Wet have been obtained over a wide range of process conditions. For example, an increase in throughput of 20 to 40% has been observed while maintaining high conversion. Intrinsic rate constants and equilibrium conversions have


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been measured. As a result of this effort, Rohm and Haas can accurately predict the performance of Amberlyst 35 Wet under a wide variety of process conditions.

**Commercial Experience**

**Background:** Lyondell Petrochemical Company was interested in finding a low cost method to increase isobutylene conversion. They decided to perform a commercial trial of the Amberlyst 35 Wet in its MTBE II unit at its Channelview, Texas complex. This unit processes FCC feed and uses a single adiabatic, recycle reactor that is computer controlled. Typical operating conditions include 10 to 15% IB, methanol/isobutylene (MeOH/IB) mole ratios from 1.0 to 1.1, inlet temperatures ranging from 100°F to 115°F, and Liquid Hourly Space Velocities (LHSV) from 3 to 5.

The Rohm and Haas research group accurately predicted the effect that process changes would have on the performance of the unit. Lyondell's computer control and monitoring of the reactor enabled on-line optimization of the process. Instantaneous data logging allowed for real time assessment and comparison to the predicted performance.

**Start-up:** The start-up procedure for the MTBE unit was carried out over a period of about one and one-half days. The catalyst was loaded in a wet state in the reactor vessel, and then back-washed. After the backwash step, the reactor was flushed with butylene feed containing 12-14% isobutylene. This was carried out at a temperature of less than 100°F.

Methanol (MeOH) was then mixed with the butylene feed to give a MeOH/IB ratio of approximately 1.0. The feed was then passed through the reactor for approximately 17 hours before the inlet temperature and flow rate were increased. At this point, the remaining water in the reactor formed t-butyl-alcohol (tBA), and this continued for some time. The temperature was again adjusted and MTBE formation began to occur. This caused a further increase in the temperature profile in the reactor. Approximately 31 hours after start-up, MTBE that met commercial specifications was formed. The IB conversion at 38 hours was 92-93%. Figure 1 shows that the primary component reaching the debutanizer was MTBE with a few percent tBA. Figure 2 illustrates the temperature profile during the initial 38 hours. The considerable exotherm that occurred at approximately 15 hours reflects the formation of MTBE.

**Operation:** As the process conditions were optimized for Amberlyst 35 Wet, the IB conversion increased over the 4 weeks following start-up to a level ranging from 94% to 97%. This is consistent with the results previously obtained at Purdue University. Particular attention was paid to the effect process variables have on IB conversion. This was a major goal of the commercial trial. Figure 3 illustrates that the inlet MeOH/IB ratio, downstream of the recycle addition, is an important parameter. Isobutylene conversion increases with an increase in the MeOH/IB ratio and declines when the ratio decreases. For MeOH/IB ratios above 1.0 upstream of the recycle addition, the increased IB conversion leads to higher effective MeOH/IB ratios downstream of the recycle addition, which will in turn increase conversion. Thus, a synergistic cycle is established. The effect is more pronounced for Amberlyst 35 Wet due to the higher IB conversion that can be achieved relative to Amberlyst 15 Wet. It is possible to attain high IB conversions with sub-stoichiometric MeOH/IB ratios upstream of the recycle addition. This was evident during an eight
day period where MeOH/IB ratios upstream of the recycle flow were below 1.0 (Figure 4) while IB conversions were constantly over 95%.

Another important aspect of the MTBE reactor unit is that the total flow rate (MeOH + Butylene Feed recycle) does not have a significant impact on conversion of IB over the ranges shown. Figure 5 shows that IB conversion is typically 95% while the LHSV is increased by 40% from 3.2 to 4.6. The minimal effect of flow rate is due to the increased activity of Amberlyst 35 Wet. To demonstrate the ability of calculations to accurately predict performance of the reactor, Figure 6 compares the predicted versus actual IB conversions for LHSV ranging from 3 to 5. It is apparent that there is close correlation between the two sets of data. Figure 7 uses the calculations to show the difference in IB conversion between the Amberlyst 35 Wet and the Amberlyst 15 Wet.

A number of other process variables have much less impact on the performance of the unit. For example, the recycle ratio directly affects the IB concentration, MeOH/IB ratio, and the Liquid Hourly Space Velocity. However, it has no direct effect on IB conversion.

After more than 11 months on stream, the unit has had no measurable decline in catalytic activity (Table 1). Selectivity to MTBE is greater than 99% and no significant concentrations of C8 dimers or dimethyl ether are formed. Maximum IB conversion remains greater than 97% at similar flow rates, IB concentrations, and MeOH/IB ratios. Assuming normal operating conditions and typical contaminant levels, Rohm and Haas expects Amberlyst 35 Wet will have a longer life than Amberlyst 15 Wet due to its higher concentration of catalytically active acid sites.

Conclusion
A commercial trial of Amberlyst 35 Wet was conducted in Lyondell Petrochemical Company’s Channelview, Texas facility. The adiabatic, single reactor system experienced conversions in a range from 94-97.6%, which is 4 to 5% greater than what would have been achieved using Amberlyst 15 Wet catalyst under similar process conditions. Rohm and Haas calculations correctly predicted isobutylene conversion over a wide range of Liquid Hourly Space Velocities. Both Rohm and Haas and Lyondell have benefited by their cooperation in conducting this trial.

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Table 1

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<tr>
<th>Time on Stream</th>
<th>% IE Conversion</th>
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<td>11</td>
<td>1%</td>
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Comparison of Maximum Conversions at 11 Months to 11 Months

Figure 7

Liquid Hourly Space Velocity

Predicted IB Conversion (Ambient 15° Well)

Actual IB Conversion (Ambient 15° Well)

Ambient 15° Well vs Ambient 15° Well IB Conversion at Phase 2, 5