TECHNICAL BULLETIN

ACE TECHNOLOGY®: IMPROVED RELEVANCE ESPECIALLY FOR RESID CRACKING

THE INFLUENCE OF THE INSIDE DIAMETER OF THE FEED INJECTION LINE ON PERFORMANCE

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OBSERVATION

The coke yield measured by ACE-Model R and R+ includes as coke the combustion products of the residual hydrocarbon film inside the feed injection tube. Inclusion of this material as coke adds a bias to the coke yield that is an artifact of the test related to injection hardware and not related to catalytic cracking. The extent of the bias depends on the properties of the feed and the inside diameter of the feed injection tube.

The coke artifact from feed holdup in the injector is measurable when processing feeds with significant fractions boiling above the cracking temperature. Feed holdup in the injector for gas oil boiling range feeds is less measurable and is a smaller artifact to the coke yield in absolute terms.

OBJECTIVE: TO ACCOUNT FOR THE “COKE ARTIFACT”

This bulletin provides a method for measuring the impact of the holdup of feed in the injector on the coke yield and on the entire yield structure.

Method:
ACE-Model R+ cracking results are presented in this report for three injectors with different inside diameters: 1.00 mm, 0.75 mm, and 0.50 mm. The data are useful for estimating cracking yields that could be obtained if the feed were supplied through injection tubes of even smaller dimension including extrapolation of the results to a hypothetical injector that in the limit has an inside diameter of zero.

The concept of an injector with an inside diameter of zero effectively subtracts the liquid holdup artifact because the surface area and volume for such a film go to zero in the limit. In addition, the use of different size injectors allows the sensitivity of the cracking yields to be examined as a function of the injector I.D.

EXPERIMENTS

Cracking Materials:
The materials used for this study are directly from a resid cracking unit in the Pacific Rim region. The feed is 22.2 API with 30% boiling above the cracking temperature of 531°C (988°F), 20% boiling above the resid cut-point 565°C (1050°F), a 95% point of 666°C (1231°F TBP), and a Conradson Carbon Residue (CCR) of 3.4 wt%. Contaminant metals on the equilibrium catalyst are 3200 ppmw V and 1900 ppmw Ni. The catalyst includes ZSM-5 additive.

ACE Operating Parameters:
The cracking experiments are performed on an ACE-Model R+ unit equipped with an Agilent 3000 RGA. The catalyst charge for each ACE run is 9.00 grams and the oil feed rate is fixed at 1.200 grams/minute. Catalyst-to-Oil is varied by changing the feed injection time. The initial catalyst temperature is set 15°C above the respective

commercial riser outlet temperature. The catalyst is fully stripped after each reaction. The ACE reactor setup consists of a standard injector position (at 28.6 mm or 1.125" from the reactor bottom). These conditions have been proven to emulate the performance of modern commercial riser reactors characterized by residence times of about 2.5-3.0 seconds.

Cracking Runs:
Six cracking runs are performed for each injector I.D. with C/O ratios from 3.0-7.5. The coke results from ACE presented here include a hydrogen-on-coke component of 6.5% of the total coke. The cracking data are presented graphically in Figures 1-16.

RESULTS AND MODELING

Figure 1: Injection Pressure During Reaction (as a function of injector I.D.)
Figure 1 shows the injection pressures observed during this study for each injector tested. It is apparent that if the feed tested were more viscous or injected faster, then it may not have been possible to collect any data with a 0.50 mm I.D. injector (with standard ACE injection hardware and gas supply pressures).

The I.D. of the standard injection tube for ACE experiments is 0.75 mm (0.030"). This dimension is probably the smallest that can be conveniently used in ACE equipment for general research on a wide variety of different oil feeds.

Figures 2-4: Modeling of the Coke Yield Versus Injector I.D.
In Figure 2 the normalized results are used to calculate the milligrams of coke yielded at 5.0 C/O for each injector size. The line in Figure 2 is derived from the regressed equations for the coke yield respective of each injector and evaluated at 5.0 C/O. Figure 2 shows that the 1.00 mm I.D. injector produces about 19.5 milligrams of coke more than a hypothetical injector of 0.00 mm I.D. on this feed at 5.0 C/O. Figure 3 is similar to Figure 2 but the data are presented as the Coke Yield (as a percent of feed) versus injector I.D.

The conversion versus C/O relationship is independent of the injector I.D. in the range of injectors studied (Figure 4). For this reason, modeling at constant C/O (Figures 2 and 3) will yield the same results as modeling at constant conversion.

Figures 5-16: Yield Results
Figure 5 shows the coke yields for the three different injectors as a function of conversion. Figure 3 shows that the coke yield decreases approximately in a linear progression with the injector I.D. (at either constant conversion or constant C/O). The linearity and slope are not significantly conversion sensitive. So, for simplicity, the change in coke yield as a function of injector I.D. at any conversion is modeled to follow the slope of the equation presented in Figure 3. This equation shows that the coke yield at 0.00 mm I.D. will be approximately 0.542 wt% of feed lower than the coke yield for a 0.50 mm I.D. injector at any given conversion. The extrapolated coke yield curve for a

0.00 mm I.D. injector is thus drawn at 0.542 wt% of feed less than the regressed coke yield curve associated with the 0.50 mm I.D. injector.

The Delta Coke plot of Figure 6 very clearly shows the impact of the injector I.D. because the data in this figure are not influenced by the variance in conversion measurements (which cause some scatter in Figure 5). There is no doubt that using smaller injectors reduces the measured coke levels at a given C/O ratio consistent with Figure 6.

Figures 7-16 present the major yields and ratios using a 221°C (TBP, true boiling point) cut-point between Gasoline and LCO and a 360°C (TBP) cut-point between LCO and Bottoms. The only yields significantly affected by injector I.D. for modeling purposes are coke and gasoline (Figures 5 and 13). The remaining yields are practically insensitive to the injector I.D. in the range studied.

In this regard, the coke yield decrease as a function of injector I.D. presented in Figure 5 results primarily in a gasoline yield increase in Figure 13. The extrapolated gasoline yield curve for a 0.00 mm I.D. injector is thus drawn at 0.542 wt% of feed more than the regressed curve for gasoline associated with the 0.50 mm I.D. injector.

At the commercial conversion, the ACE coke yield projected for an injector with 0.00 mm I.D. is 6.30 wt% and essentially matches the commercial coke yield of 6.48 wt% as shown in Figure 5. Without the correction for injector I.D., the coke yield determined by ACE-Model R+ is 7.12 wt% (10% higher than the commercial result).

Figure 5 shows that all of the injectors tested make more coke than the commercial unit at the commercial conversion. It is this tendency or bias that precipitated this study. A film thickness inside the 0.75 mm I.D. injector of 0.0005-0.001” could account for the applied coke yield correction that is made here by estimating the performance in the limit of a 0.00 mm I.D. injection tube.

At 5.0 C/O, the correction in coke from the 0.75 mm I.D. injector takes 14.6 mgms from the coke yield and reallocates it to gasoline. This 14.6 mgms is out of 1800 mgms of feed: so this is a relatively fine issue being resolved by this study. Finally, it does appear that the holdup depends on C/O for the ACE operating protocol of this study. Lower C/O involves larger feed mass which will cool the injection tube to a greater extent: the lower the temperature of the tube the greater the film thickness inside the injector.

CONCLUSIONS AND RECOMMENDATIONS

This bulletin presents a noteworthy artifact of the ACE test. Moreover, it shows that the need for improving the relevance of ACE on coke yield for high boiling range and high CCR feeds does not necessarily require short injection times. Instead, it requires an understanding of both the feed holdup in the injector and perhaps the implications of feed atomization of oils that have a significant non-vaporized fraction at cracking temperatures.

With the data and method described here, ACE users can understand why high boiling range feeds (especially with high viscosity) tend to give higher coke yields in ACE-Model R and R+ units than in the commercial units at the same conversion. Moreover, such offsets on difficult feeds may be corrected in a scientific manner thus providing ACE results that are more accurate with respect to both coke and overall yields.

The method and data of this report improve the understanding of the performance of the ACE-Model R and R+ units. There are two important issues here:

- From a catalyst evaluation perspective, the “coke artifact” is independent of the catalyst system. In this regard, the “coke artifact” for a given feedstock represents a direct systematic error that affects all catalysts equally and therefore does not affect catalyst ranking.

- From a feedstock evaluation perspective, the “coke artifact” is a concern because (if ignored) it will make high boiling range feeds appear to be higher coke yield producers than is actually the case. In this regard, the “coke artifact” can be characterized as a systematic error with a bias favoring feedstocks that would not produce a significant holdup in the injector.

The dominant effects of using smaller injectors are improved coke selectivity (Figures 3 and 5), a shift to lower delta coke (Figure 6), and a shift to higher gasoline selectivity (Figures 13 and 14). The magnitude of the shifts depends on the feed properties. For the feed of this study, the shift in coke yield at constant conversion from the standard injector of 0.75 mm I.D. to a hypothetical injector of 0.00 mm I.D. is from 7.12 wt% to 6.30 wt% (a decrease of ~12%). For more difficult high-boiling-range feedstocks it seems plausible that the shift in the coke yield between a 0.75 mm I.D. injector and a 0.00 mm I.D. injector could exceed 25%.

Kayser Technology, Inc. (KTI) is not advocating the use of smaller I.D. injectors for normal ACE operation because the pressure drop is too high (Figure 1). Obtaining data for the 0.50 mm injector may not be possible for many difficult feeds. In addition, KTI does not currently recommend a different injector design for ACE: the relatively long injection tubes play an important role for feed preheat and vaporization and the standard 0.75 mm I.D. provides long life with an acceptable pressure drop.

ACE users interested in quantifying the “coke artifact” should consider an alternative to the method of this report that does not require the use of different I.D. injectors. (See “An Alternative Method to Account for the Coke Artifact” below.)

Over time, it may be possible to model the injector holdup to an extent that a correction may be applied to the data directly. This is a complex subject, however, because the physical properties influencing the thickness of the film are of the non-vaporized feed at temperatures around 540°C (~1000°F).

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PERSPECTIVE

The coke correction described here represents a new tool that has significant implications because the development of FCC laboratory tests over the years has been influenced by the bias of test results towards higher coke yields on difficult feeds.

High coke yields drove some researchers in the direction of altering test conditions to shorter feed injection times. This follows the line of thinking that shorter injection times are required for the purpose of reducing “feed on-time” and thus reducing the coke yield in batch tests (Voorhies coke kinetics).

Many ACE users have changed the feed injection rate on ACE from 1.20 grams/min to 2.40 grams/min to effectively reduce the feed on-time by 50%. While I am not certain how this has improved the relevance of the measured coke yields, it certainly does not account for the part of the coke yield that is an artifact related to the injection hardware. That artifact still exists at 2.40 grams/min feed rate.

Now, this work isolates the injection hardware as a major source of the coke bias in ACE Model R and R+ units when cracking difficult feeds. So, one must wonder if there was ever any need to reduce the feed on-time when the data at the standard feed rate of 1.200 gms/min does not exhibit a coke bias after it has been corrected for the “coke artifact” related to feed holdup in the injector (refer to Figure 5).

There are two important points to consider:

- The close correspondence of ACE results with commercial units operating on gas oil boiling range feeds indicates that the cracking mechanisms occurring in ACE mimic those of continuous riser cracking. This holds true for the KTI recommended 1.200 gms/min feed rate, but sometimes requires an injector position adjustment to accommodate different riser residence times. ACE users have tracked numerous commercial units through catalyst changes involving shifts in Z/M ratio and different catalyst materials and additives, as well as changing feedstock quality. ACE has shown no bias in favor of one catalyst system or another and no bias towards varying gas oil properties. ACE simply agrees with the commercial performance through all the normal variations.

- The same cracking mechanisms occurring in ACE reactors that hold for gas oil feeds must also hold for resid containing feeds. Because the feed boiling range is higher is not a compelling reason to alter the ACE test (or any test) when handling a resid containing feed. A good test should work on any FCC feed. Unfortunately, about ten years ago the coke yields measured in ACE (and other lab cracking units) with resid containing feeds were 10-30% higher than the corresponding commercial coke yields (depending on the difficulty and viscosity of the feed). A quantitative understanding of the source of this bias was missing. For sure, the holdup of feed in the injector is a large part of the problem – and perhaps atomization is another part (but this component was not exposed here).

This report brings the understanding of ACE operations to a higher level and bridges "the performance gap" between data obtained on gas oil and resid feeds.

AN ALTERNATE "METHOD" TO ACCOUNT FOR THE "COKE ARTIFACT"

Kayser Technology, Inc. has performed cracking runs in Model R+ and discharged the spent catalyst prior to an *in situ* regeneration. After the spent catalyst discharge, the reactor is regenerated and the residual hydrocarbon in the reactor is burned and accounted for by the Model R+. The amount of carbon measured is very similar to the coke yield correction made in this report (albeit with different feed material). This brief test led to the injector I.D. study presented here.

The ACE-Model R+ MM (Multi-Mode) is probably the preferred machine for quantifying the coke correction without changing the injector I.D. The operation is done as follows: ACE data with full catalyst regeneration could be obtained first. Then, a sequence of runs could be performed with spent catalyst discharge followed by reactor regeneration as described above. The residual carbon coming from the reactor's injector after spent catalyst discharge could be subtracted from the associated full burn coke yields and the same residual (for simplicity) could be added back to the gasoline yield in a way similar to this report. For Model R+ users, this capability will require an upgrade to ACE-Model R+ Multi-Mode (which has other valuable features, too).

COMMENTS ON RELATED TESTS

ACE-MODEL AP

Model AP is designed primarily for processing gas oil feeds (although some labs use higher boiling feeds). Since the Model AP does not perform *in situ* regeneration, the coke yield does not include the "coke artifact" of feed in the injector. Model AP measures coke directly on the catalyst only. So, on a relative basis, one can expect Model AP to measure lower coke yields than Model R and R+: which is the case. But, this may be hard to see if both are processing gas oils and would require the carbon analysis to be well calibrated to detect the difference.

If different injector I.D.s are used on the ACE-Model AP (which does not have *in situ* regeneration) the coke yield data would not be influenced by liquid holdup in the injector. So, any data shifts would be related to liquid droplet size from smaller I.D. injectors. Based on the data of this report, there is considerable doubt the Model AP yields would be very sensitive to injector I.D. for the range of injector diameters presented here.

PULSE TESTS:

Some researchers have resorted to pulse tests that effectively supply the feed into a reactor in a second or two. This represents the extreme case of the argument that feed on-time must be short. Several years ago, KTI developed a pulse test with a special reactor designed to overcome the problems of other pulse tests. Experiments using feed injection times from 0.50-3.00 seconds may be performed on this platform. The results obtained thus far are not compelling enough to commercialize the technology against current ACE Technology®.

ACKNOWLEDGEMENTS

Kayser Technology, Inc. is grateful to the Research Laboratory of Intercat-Savannah for making available to KTI an ACE-Model R+ unit specifically for this study and for providing precise Simulated Distillation analyses of the cracked liquid products.

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FIGURE 1
INJECTION PRESSURE DURING REACTION
FEED RATE OF 1.20 GRAMS/MIN
3.4 CCR FEED WITH 20% BOILING IN THE RESID RANGE

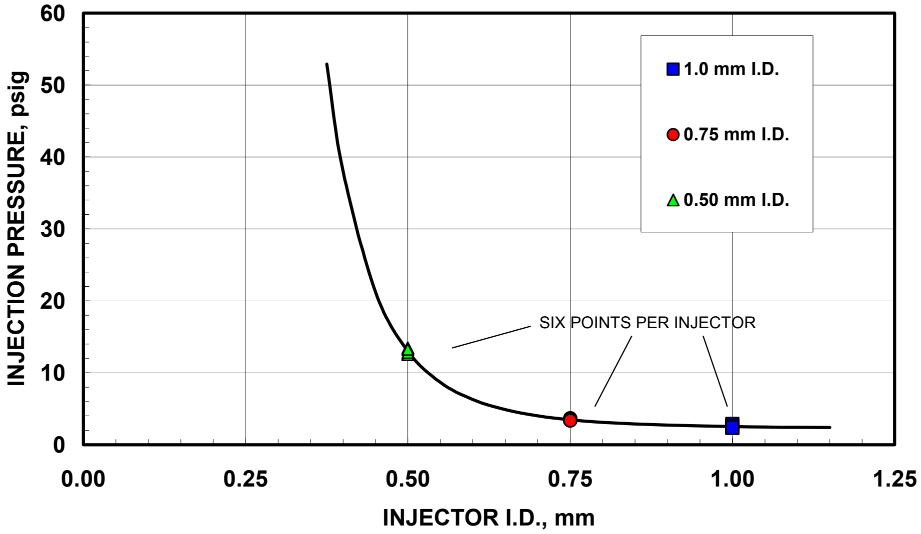

FIGURE 2
MILLIGRAMS COKE YIELD VERSUS INJECTOR I.D. AT 5.0 C/O
(9.0 GRAMS OF CATALYST, INCLUDES H-ON-COKE OF 6.5%)

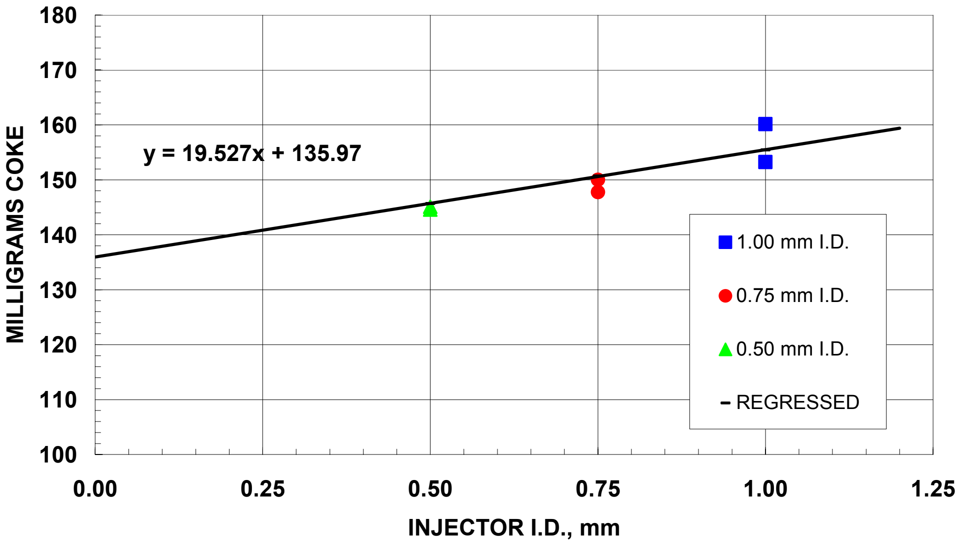

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FIGURE 3
COKE VERSUS INJECTOR I.D. AT 5.0 C/O

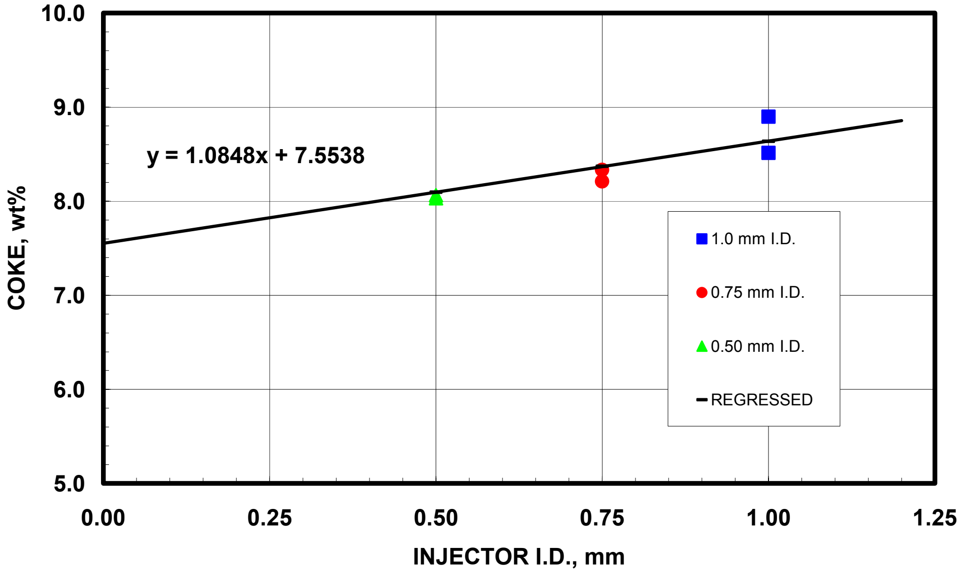

FIGURE 4
ACTIVITY: 221°C+ CONVERSION -vs- CAT/OIL RATIO

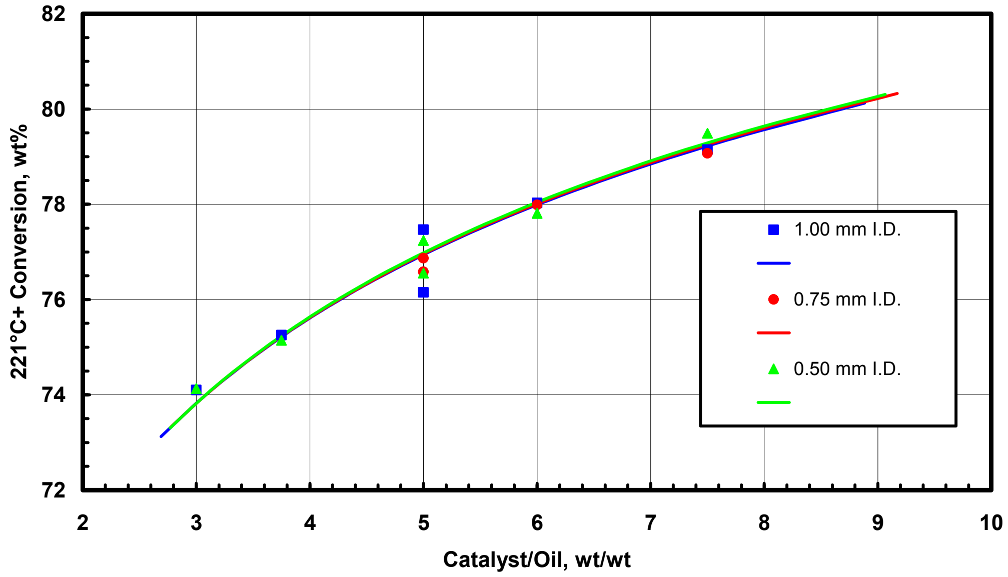

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FIGURE 5
COKE YIELDS -vs- 221°C+ CONVERSION

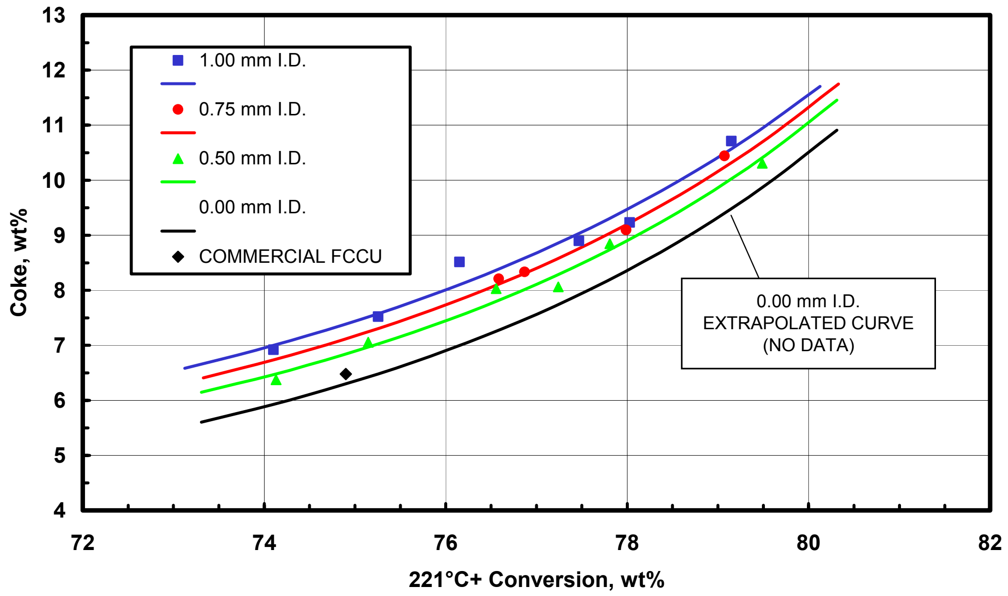

FIGURE 6
DELTA COKE -vs- CATALYST/OIL

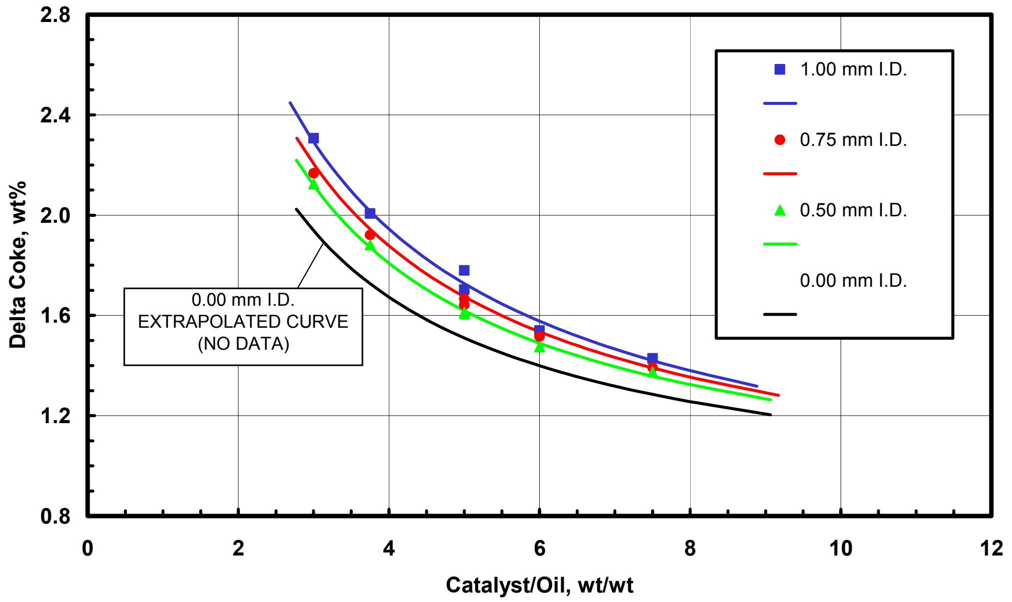

FIGURE 7
DRY GAS YIELDS -vs- 221°C+ CONVERSION

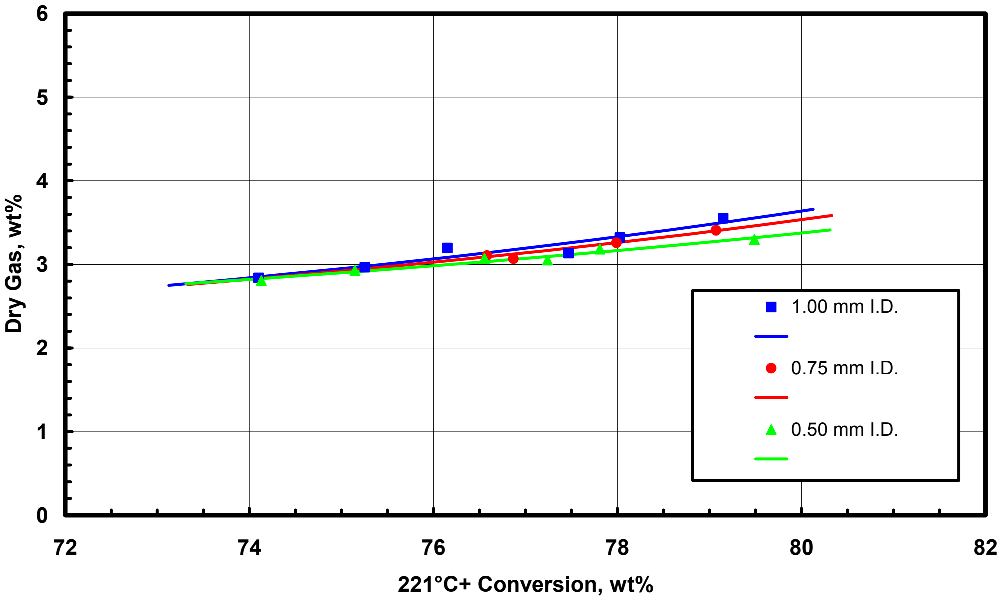

FIGURE 8
LPG YIELDS -vs- 221°C+ CONVERSION

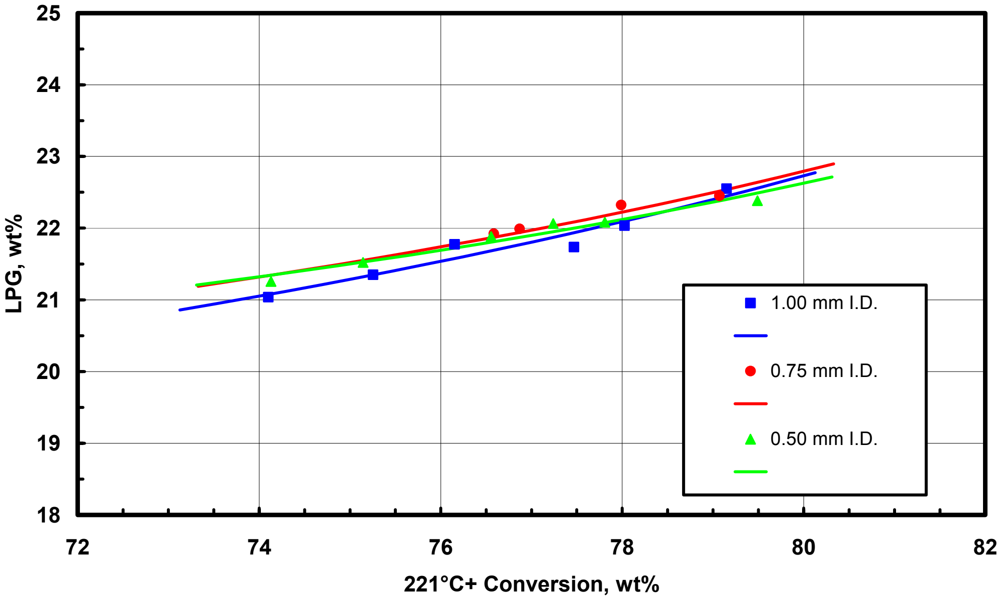

FIGURE 9
PROPYLENE YIELDS -vs- 221°C+ CONVERSION

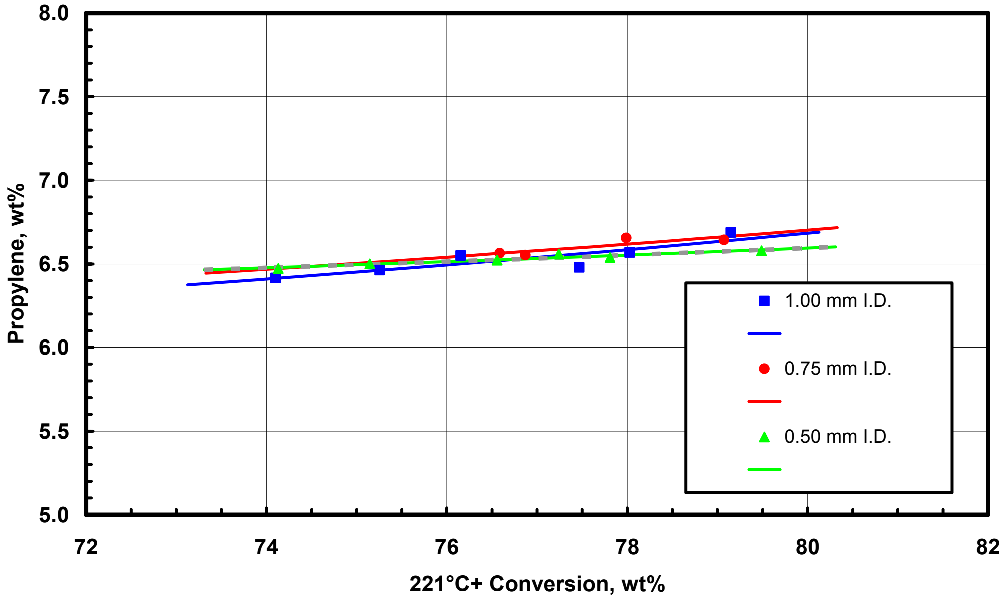

FIGURE 10
C3=/TOTAL C3s -vs- 221°C+ CONVERSION

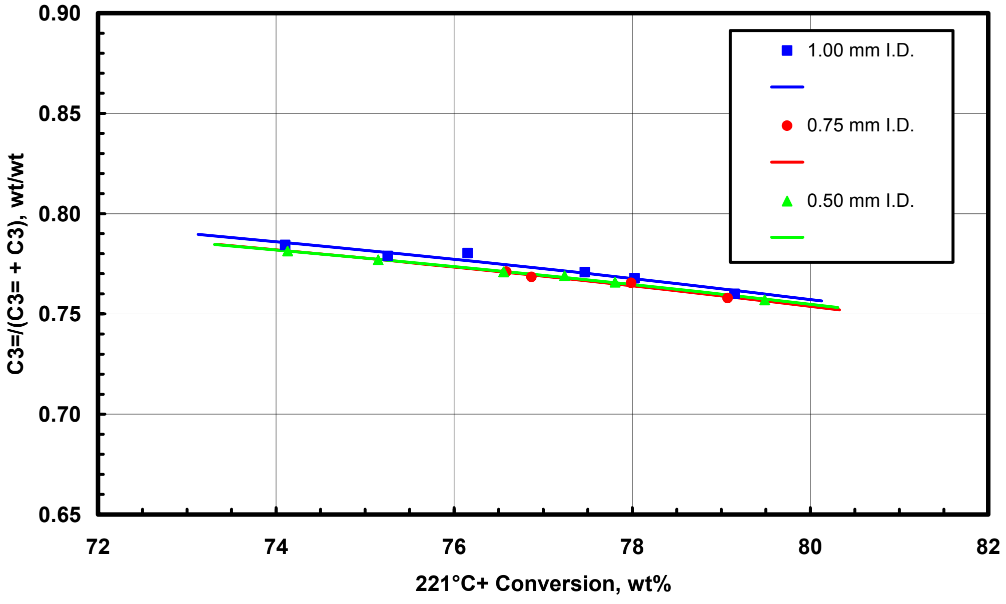

FIGURE 11
C4 OLEFINS YIELDS -vs- 221°C+ CONVERSION

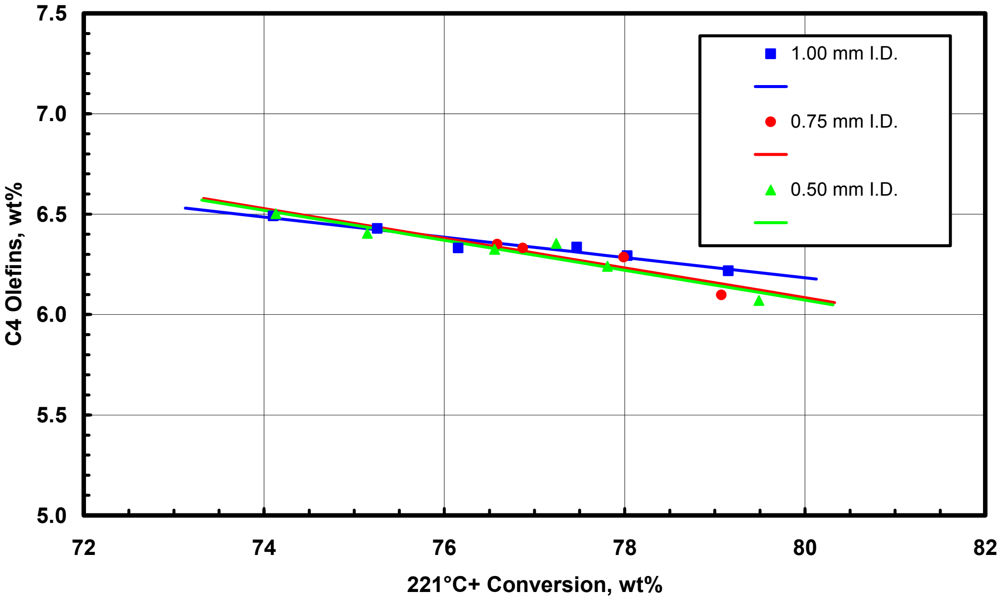

FIGURE 12
C4=/TOTAL C4s -vs- 221°C+ CONVERSION

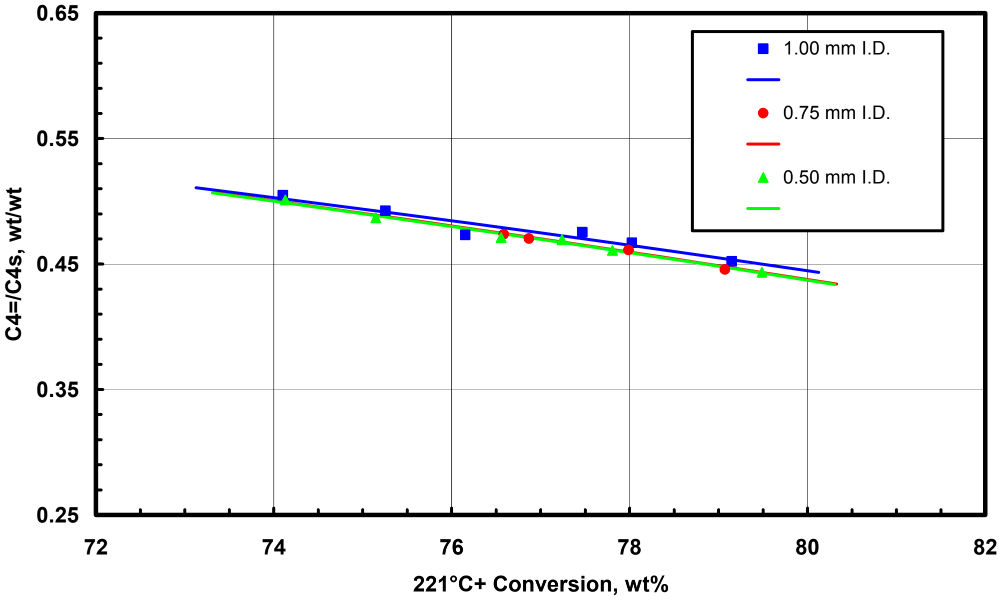

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FIGURE 13
GASOLINE YIELDS -vs- 221°C+ CONVERSION

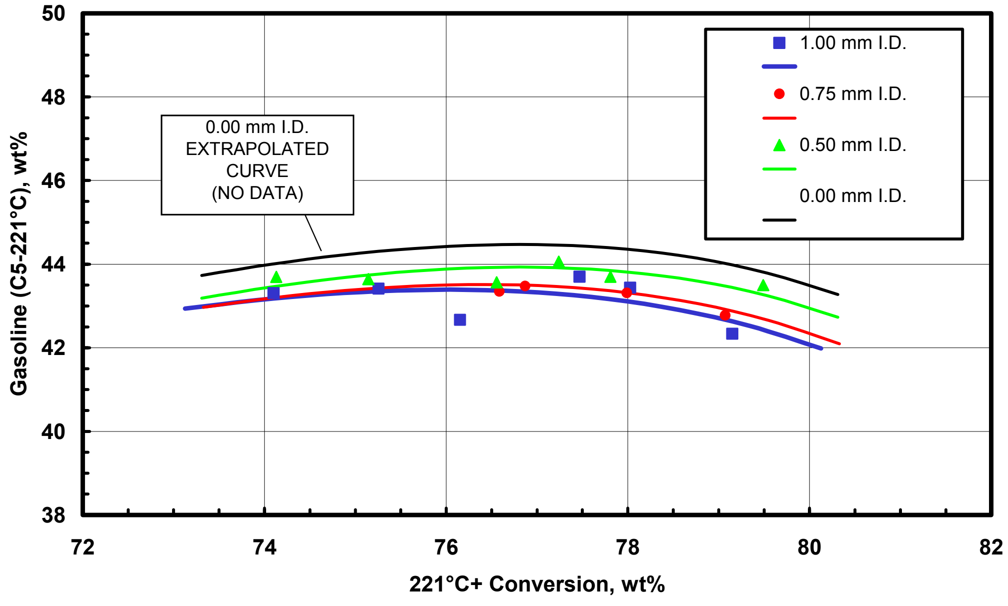


FIGURE 14
GASOLINE SELECTIVITY -vs- 221°C+ CONVERSION

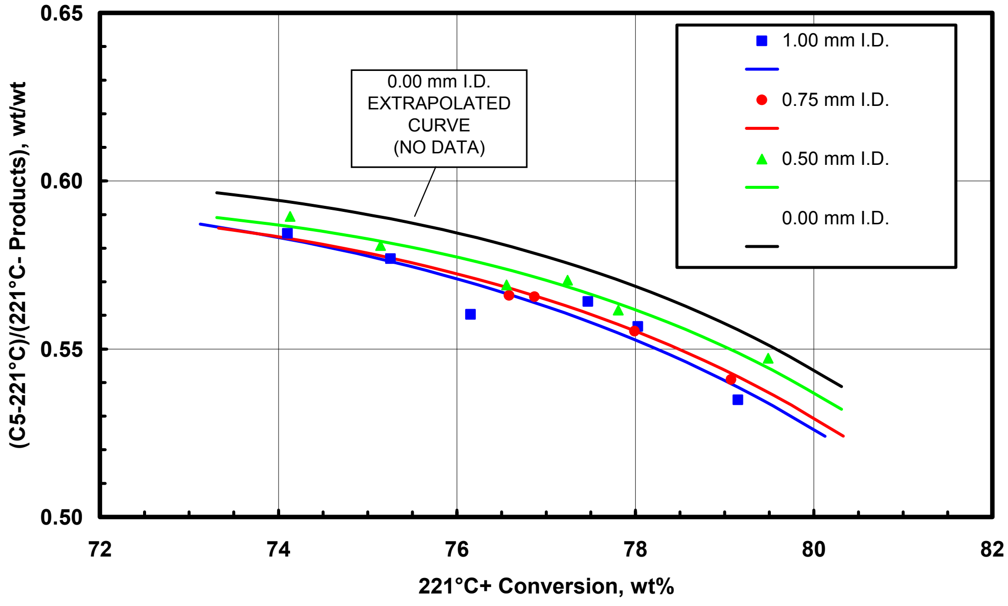


FIGURE 15
LCO YIELDS -vs- 221°C+ CONVERSION

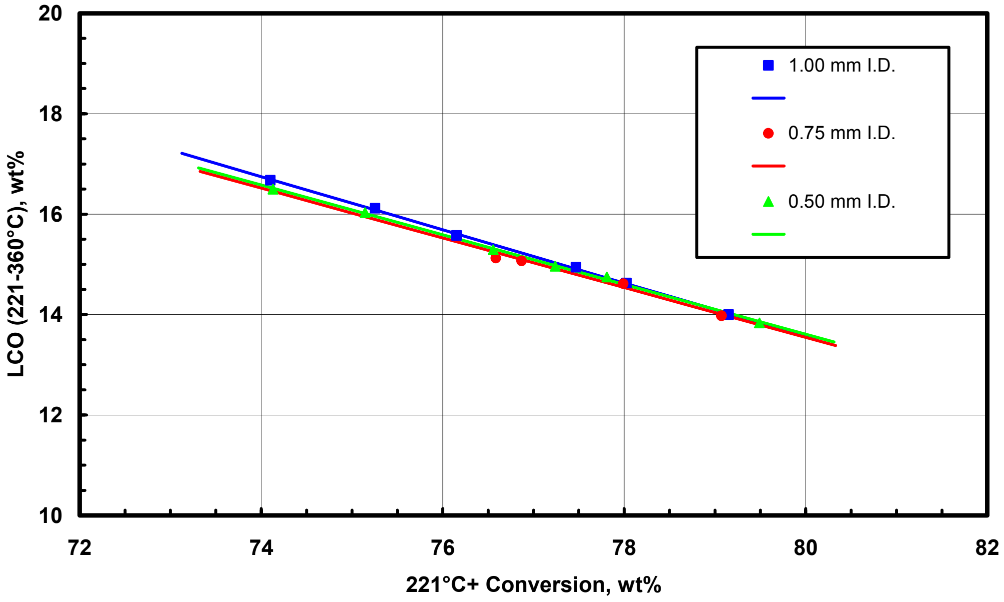
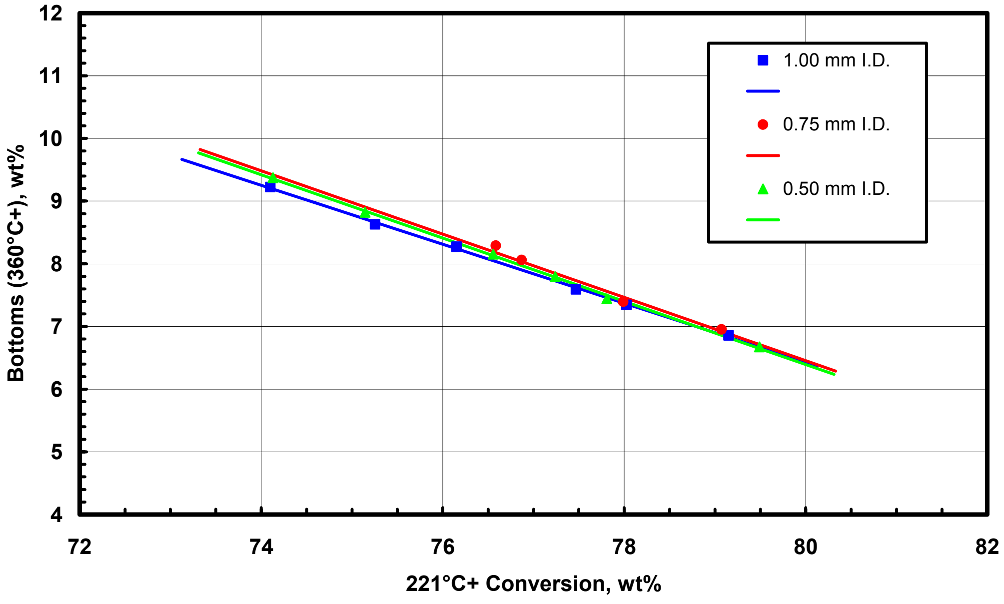


FIGURE 16
BOTTOMS YIELDS -vs- 221°C+ CONVERSION



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