

3.3.4.3 Comparison of Reactor Solvents (C-30 oil vs PW_R3000 Wax)

This series of runs involves comparing the performance of a high molecular weight polyethylene wax, Polywax PW_R3000, for use as a reactor solvent, to that of the typically used C-30 oil. For this comparison, the well studied 4.4Si150 cyclone catalyst was used (4.4atomic%Si and 1.0atomic%K, both relative to Fe, i.e., [Si(or K)]/[Si(or K) + Fe]). 32.22g of the catalyst was used in all of the runs, and for the C-30 oil application the catalyst loading was at 10.0wt%, while for the PW_R3000 wax a 11.1wt% catalyst loading was used. This difference in weight% loadings stemmed from attempts to establish equivalent volumes of solvent during the initial loading of the continuously stirred tank reactors (CSTR). These runs were modeled after previous runs that used the C-30 oil as a solvent, which were normally loaded at a 10.0wt% catalyst loading, specifically 32.22g of catalyst along with 290.0g of C-30 start up oil/solvent. With the density of the C-30 oil at ~0.80g/cm³, this yielded a start up solvent volume of 362.5cm³, thus the target volume for the PW_R3000 wax was 362.5cm³. As the PW_R3000 wax is a solid at ambient temperatures, it was heated until it melted, i.e., at ~130°C, at which point the density was determined to be 0.71g/cm³. Thus at 130°C, it requires 257.4g of PW_R3000 wax to obtain a volume of 362.5cm³. Note that the density of the C-30 oil should have been determined at a temperature of 130°C, instead of at ambient temperature (at a later date the densities and specific volumes(cm³/g) of the PW_R3000 and C-30 oil were determined up to 210°C, as well as the densities and specific volumes for the C-28 (octacosane) and the PW_R2000 high molecular weight polyethylene wax, and that algorithms were then developed for the densities and specific volumes as a function of temperature from ambient through 210°C).

Run LGX248 was performed as the baseline case with the C-30 oil and the %CO conversion results are given in Figure 1. The %CO conversion results for the PW_R3000 run, LGX249, are shown in Figure 2. Both reactor solvents produced CO conversions of 80-90%, until gas feed tube pluggages occurred (at ~run hour 550 for the C-30 oil and at ~run hour 460 for the PW_R3000 solvent). These two runs showed the feasibility of using the PW_R3000 polyethylene wax as a reactor solvent. It was then decided to repeat the PW_R3000 run to confirm the reproducibility of the results obtained in run LGX249. Run LGX251 was started and it was observed that the pretreatment pressure had climbed to ~40psig (pretreatment is to be carried out for 24 hours at 0psig), but aborted after two days at synthesis conditions. Thus run LGX252 was initiated, but it too was aborted after three days at synthesis conditions, due to a pressure of ~100psig during the pretreatment period. It was discovered that the reason for the elevated pressures during the pretreatment period was caused by the restriction of the gas out and due to blinding off and/or plugging in the 7 μ -wax filter and the wax line out of the reactor, which functions as a continuous line out for the gas products produced during the FTS reaction. It was found that the restrictions were caused by the condensing and solidifying of the PW_R3000 polywax (melting point at ~130°C) which possibly had been entrained in the gas out of the reactor via the wax line out. To rectify this problem, the wax filter was fitted with a thermocouple and an additional heat tape was installed on the wax line, as well as increasing the amount of insulation on the wax line out (this was also done for the re-wax line out to allow for the removal of the reactor liquid products). This allowed for the monitoring and adjustment, if necessary, of the temperature of the 7 μ -wax filter and wax line. After these modifications, run LGX253 was started and the pretreatment period was successfully completed at the desired pressure of 0psig.

Figure 3 gives the %CO conversions for runs LGX251, LGX252, and LGX253 and shows an inverse relationship with %CO conversion and pretreatment pressures. Note that the %CO conversion for run LGX253 agrees rather well to that of the %CO conversion for run LGX249. That is, for run LGX253 the CO conversion starts at ~90% and is maintained at ~85% or greater up through run hour 500. It was thus shown that the PW_R3000 polyethylene wax could be used as a suitable reactor solvent for the FTS synthesis.

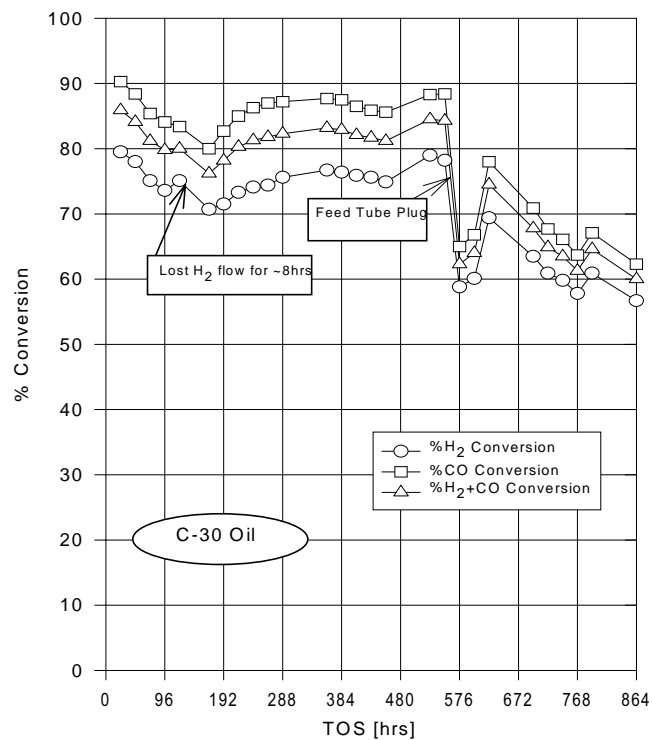


Figure 1. %CO Conversion vs Time on Stream [TOS] for Run LGX248_{R1}.

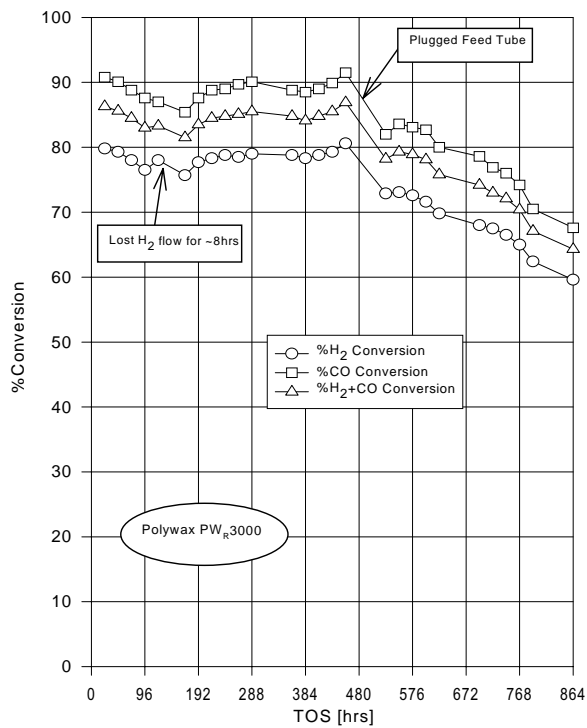


Figure 2. %CO Conversion vs Time on Stream for LGX249_{R2}.

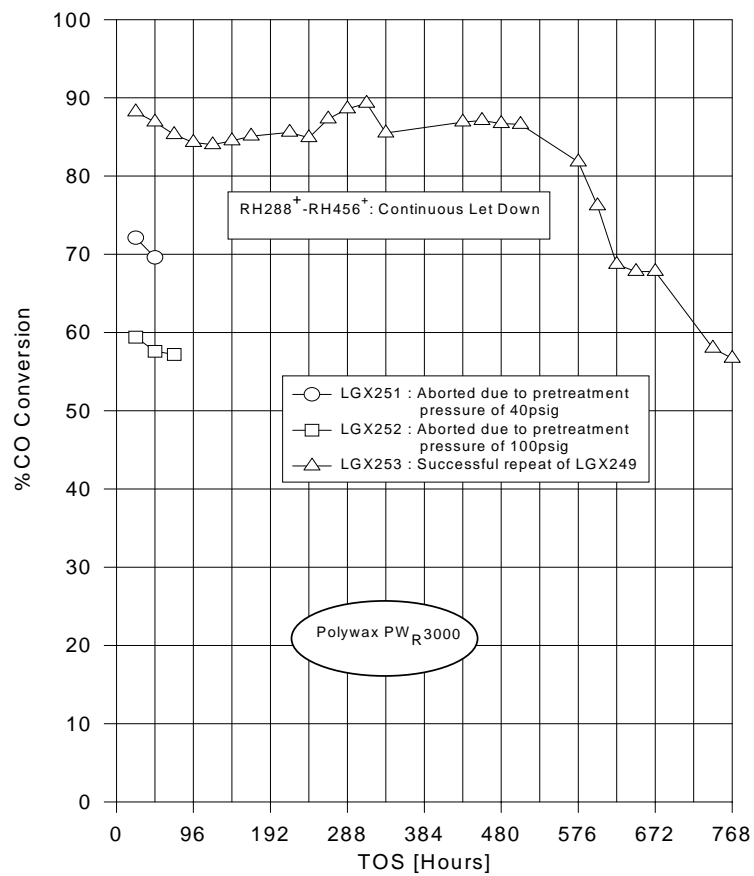


Figure 3. %CO Conversion vs Time on Stream for Runs LGX251-253.

3.3.4.4 Comparison of Alumina and Silica Based High-Alpha Catalyst at 230°C and 250°C

Once it was shown that the Polywax PW_R3000 was a suitable reactor solvent, five Fe-based/silica catalysts and five Fe-based/alumina catalysts were tested at both 250°C and 230°C for their conversion performance in the one liter continuously stirred tank reactors (CSTR). The ten catalysts tested at the two synthesis temperatures are referred to as the hi-alpha catalyst studies. All catalysts were activated with syngas (H₂/CO = 0.7) at 270°C, ambient pressure and a space velocity of 3.11 (STP) h⁻¹ g-Fe for 24 h. The reactor pressure was increased to 1.3 MPa after activation and FT synthesis was started. The alumina and silica series catalysts were both co-precipitated with the iron such that atomic ratios of aluminum(silicon) relative to Fe was 0.044 or, 4.4atomic% Al(Si). All ten catalysts were impregnated with copper so that the copper was present at a 3.0wt%Cu, relative to iron. Both the silica and alumina series Fe-based catalysts had varying amounts of potassium, specifically 0.0wt%K, 2.5wt%K, 5.0wt%K, 7.5wt%K, and 10.0wt%K, relative to Fe. The following list identifies the catalyst and gives an atomic(mole) representation of the Si/Al, Cu, and K, based on 100 atoms/moles of Fe.

Silica Series:

RJO228(0.0wt%K) 100Fe:4.60Si/2.72Cu/0.00K

RJO229(2.5wt%K) 100Fe:4.60Si/2.72Cu/3.66K

RJO230(5.0wt%K) 100Fe:4.60Si/2.72Cu/7.52K

RJO231(7.5wt%K) 100Fe:4.60Si/2.72Cu/11.58K

RJO232(10.0wt%K) 100Fe:4.60Si/2.72Cu/15.87K

Alumina Series:

RJO250(0.0wt%K) 100Fe:4.60Al/2.72Cu/0.00K

RJO251(2.5wt%K) 100Fe:4.60Al/2.72Cu/3.66K

RJO252(5.0wt%K) 100Fe:4.60Al/2.72Cu/7.52K

RJO254(7.5wt%K) 100Fe:4.60Al/2.72Cu/11.58K

RJO255(10.0wt%K) 100Fe:4.60Al/2.72Cu/15.87K

The silica series catalysts at a synthesis temperature of 250°C were tested first and Figure 1 shows the %CO conversion versus time on stream. These runs were designated as LGX254-258 and used the RJO232, RJO231, RJO230, RJO229, and RJO228 catalyst, respectively. The %CO conversion for the silica series at 230°C is presented in Figure 2 (runs LGX259-263 utilizing the RJO232-228, respectively).

For the alumina series at 250°C, the CO conversion is given in Figure 3 (runs LGX267-271 utilizing the RJO250, RJO251, RJO252, RJO254, and RJO255 catalysts, respectively) while Figure 4 shows the %CO conversion for alumina at 230°C (runs LGX276-279 using the RJO251, RJO252, RJO254, and RJO255 catalyst, respectively, and run LGX283 using the RJO252 catalyst). Note that for the 230°C alumina series that the catalyst with 0.0wt%K was not tested and that run LGX283 is a repeat run of LGX277 (the 5.0wt%K catalyst). Also note for runs LGX276, LGX278, and LGX279, at ~run hour 183, a re-pretreatment of the catalysts with only CO gas was performed, which did not appear to help.

In general, the following trends were observed for the %CO conversion,

- ☞ For Both 230°C and 250°C Synthesis Temperatures

- Silica Series Better Than Alumina Series

- ☞ For Both Alumina and Silica Series

%CO Conversions Better at 250°C than at 230°C

☞ For The Alumina Series

230°C : 2.5wt%K \approx 5.0wt% > 7.5wt%K > 10.0wt%K

250°C : 2.5wt%K >> 5.0wt%K > 7.5wt%K >> 10.0wt%K > 0.0wt%K

☞ For The Silica Series

230°C : 7.5wt%K \geq 5.0wt% \geq 2.5wt%K >> 10.0wt%K > 0.0wt%K

250°C : 2.5wt%K \geq 5.0wt%K \geq 7.5wt%K >> 10.0wt%K > 0.0wt%K

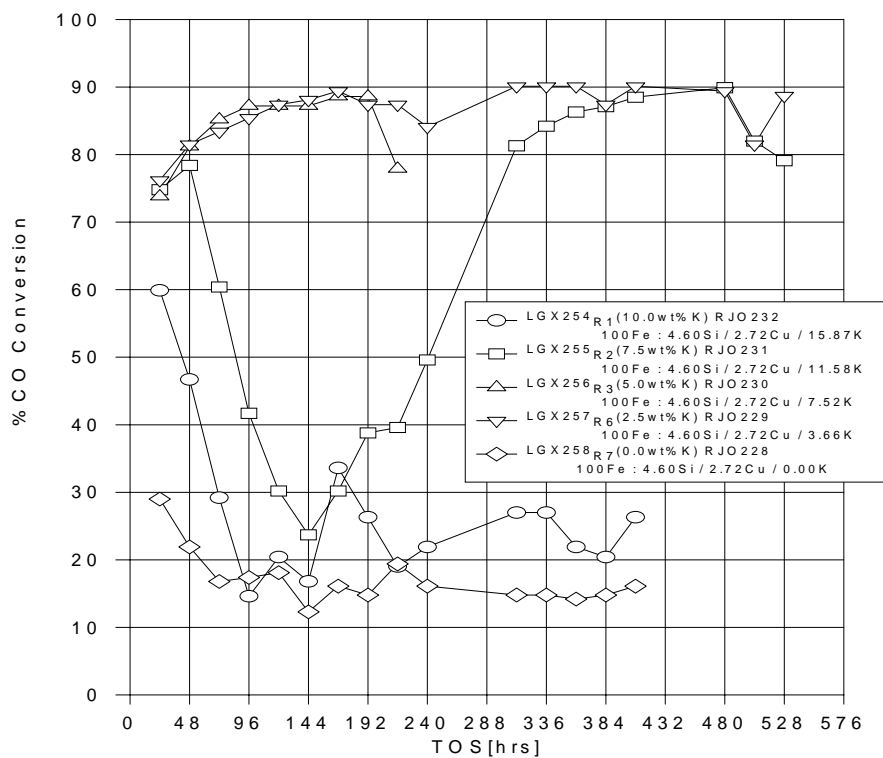


Figure 1. %CO Conversion vs Time on Stream for Runs LGX254-258.

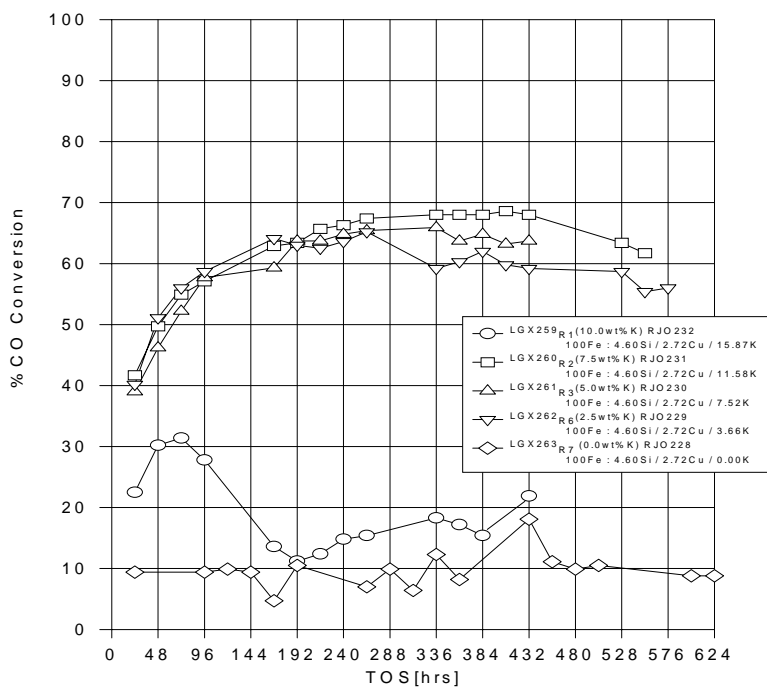


Figure 2. %CO Conversion vs Time on Stream for Runs LGX259-263.

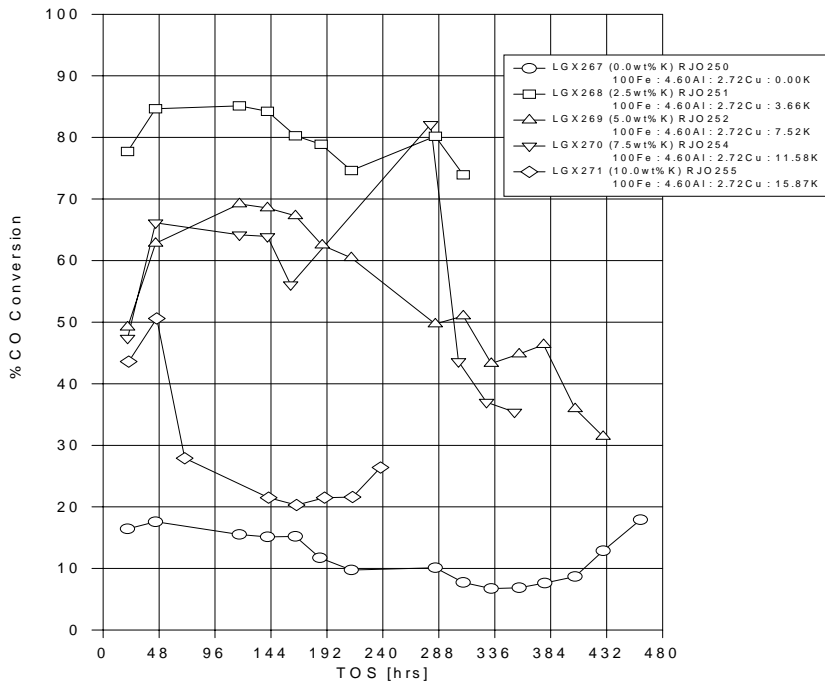


Figure 3. %CO Conversion vs Time on Stream for Runs LGX267-271.

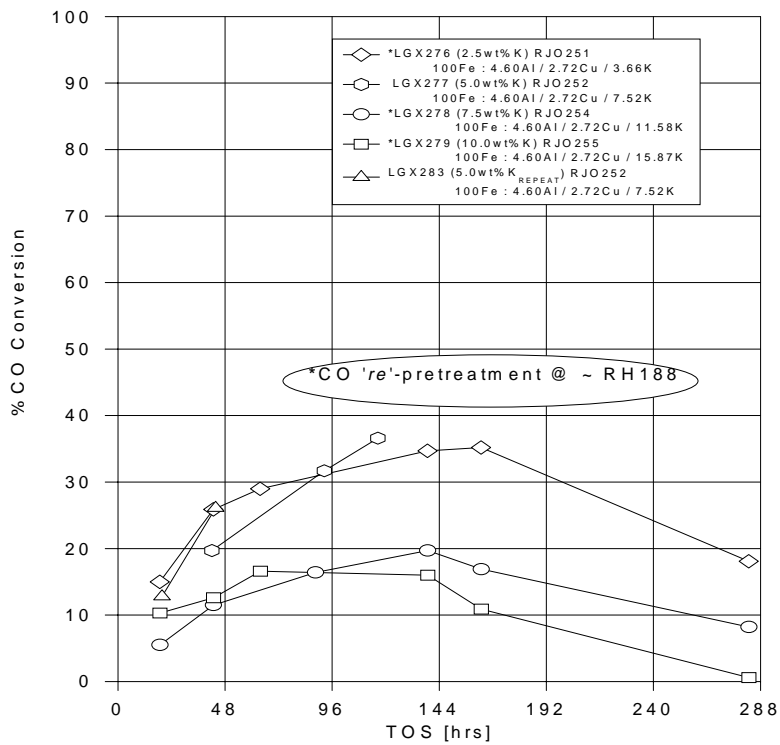


Figure 4. %CO Conversion vs Time on Stream for Runs LGX276-279 & LGX283.

3.3.4.5 High-Aluminas

A series of runs was performed using catalyst that contained varying amounts of alumina as a support. The alumina, Al_2O_3 , varied nominally from ~10wt% to ~53wt% for the four catalysts used in this series of runs and each catalyst had different amounts of Al, Cu, and K. The reactors had a 10.0wt% catalyst loading in the PW_R3000 polyethylene wax reactor solvent and a synthesis temperature of 270°C was used for these runs. The following list identifies the catalyst and gives an atomic(mole) representation of the Al, Cu, and K, based on 100 atoms/moles of Fe.

- a. RJO274 (10.15wt% Al_2O_3 & 52.69wt%Fe), 100Fe:21.1Al/2.73Cu/11.8K
- b. RJO275 (17.74wt% Al_2O_3 & 46.93wt%Fe), 100Fe:41.4Al/2.72Cu/11.6K
- c. RJO276 (37.58wt% Al_2O_3 & 35.19wt%Fe), 100Fe:117Al/2.72Cu/11.6K
- d. RJO277 (53.13wt% Al_2O_3 & 23.47wt%Fe), 100Fe:248Al/2.74Cu/11.6K

Figure 1 shows the %CO conversion for runs LGX284, LGX285', LGX286 and LGX287, which used catalysts RJO274, RJO275, RJO276, and RJO277, respectively.

Run LGX284 was aborted after 144 hours on stream due to the inability to withdraw liquid reactor product through the 2 μ -rewax filter, which is located inside the reactor and submerged in the catalyst/wax reactor slurry at start up . It is not certain if the 2 μ -rewax filter for LGX284 was blinded off from previous runs or if the tubing run from the reactor to the rewax trap (vessel for the collection of liquid reactor product) was plugged, or a combination of both. Modifications to the tubing run from the reactor to the rewax trap have been implemented to allow for a repeat of this run.

Run LGX285' was a repeat run of LGX285, as LGX285 was aborted during the 24 hour pretreatment period due to the reactor pressure rising to ~400psig (as the pretreatment pressures are fixed at a nominal 0psig).

Although there was an inability to remove reactor product via the rewax filter for run LGX284, difficulties in catalyst/wax separation and reactor product removal was not encountered for runs LGX285'-287. In fact, there was no plugging or blinding off of the rewax filters over the course of these runs and the reactor product removed through the rewax filter was visibly free from catalyst contamination. The increased amounts of Al_2O_3 and the lower Fe content associated with these catalysts are thought to be mainly responsible for the ease of reactor product removal through the rewax filter. This, along with the fact that there were problems associated with the mass balance resulted in removal of too much reactor product via the rewax filter for runs LGX285'-287. Specifically, after the completion of these runs, the reactor contents were collected and measured and deficits of 84g, 186g, and 213g from the initial catalyst/ PW_R 3000 wax loading of 344.0g was found for runs LGX285', LGX286, and LGX287, respectively. In effect, this results in higher percentage catalyst loadings for these runs, as well as a reduced residence time in the reactor slurry, but the effect on CO conversion is not well understood.

The previously mentioned problems present some difficulty in attempting to compare this series of runs, but with respect to the data for %CO conversion over time, the best results were obtained using the RJO276 catalyst (run LGX286) as CO conversions were maintained at levels of 70-80%. The CO conversion for runs LGX287(RJO277) and LGX285(RJO275) were comparable to one another for run hours 100-336, but both had CO conversions of 40% at run hour 336 while for run LGX286, the CO conversion was at +70%.

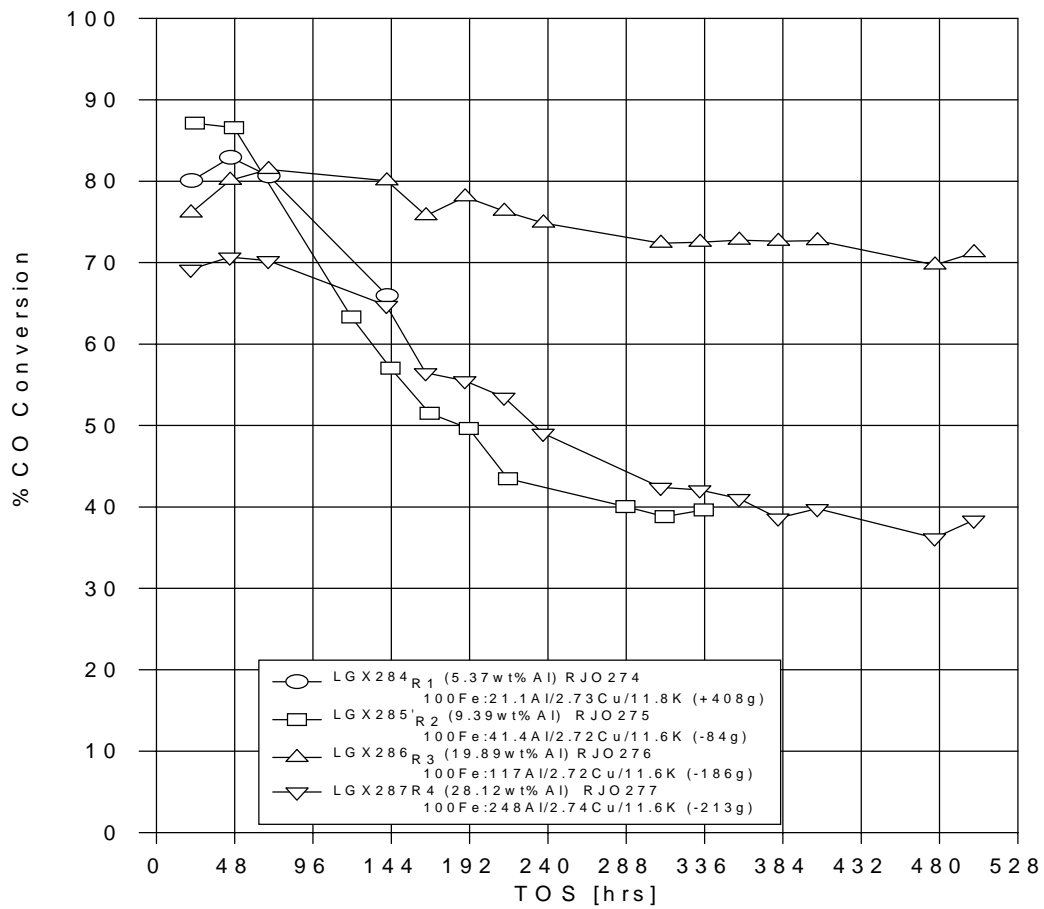


Figure 1. %CO Conversion vs Time on Stream for Runs LGX284-287.

3.3.4.6 Reactor Wax Withdrawal Modifications

In the past, reactor product and catalyst separation has been accomplished using a $\frac{1}{2}\mu$ -grade Mott Metallurgical Corporation sintered stainless steel filter ($\frac{1}{2}$ "OD and $\frac{7}{8}$ " in length for a surface area of 0.0109ft²). This filter was positioned so that when it is installed to the reactor head that it's bottom surface is ~3" down from the upper internal surface of the head of the one-liter CSTR, which has an internal diameter of 3" and an internal height of 10 $\frac{1}{4}$ ", with a hemispherical bottom and a cylindrical shaped top. Since using the Polywax PW_R3000 hi-molecular weight wax as a reactor solvent (LGX249 first PW_R3000 run) problems have persisted in that the filter was increasingly being blinded off, resulting in an increasing inability to remove the reactor product (i.e., the heavy liquid product at reactor temperature and pressure referred to as 'rewax'), allowing the reactor to fill up, ultimately resulting in aborting the runs. Potential solutions to this problem have been suggested and/or implemented.

The first of the solutions which has been incorporated, was to lower the filter to insure that it is completely immersed in the wax/catalyst slurry. The thinking here is that with the filter immersed in the slurry, it would be out of the gas/froth space (which may or may not contain smaller ebullated catalyst particles) and would be continually washed by the slurry and eliminate or at least minimize the blinding off of the filter. To accomplish this end, the filter was lowered to an elevation so that it's bottom surface is ~7" below the upper surface of the reactor (specifically, the bottom of the filter is positioned ~ $\frac{1}{4}$ " above the upper surface of the gaspersator blades). At this elevation there is no doubt that the filter is covered by the slurry for the current loadings of PW_R3000 polywax and hi-alpha catalysts. The first run using this lowered filter configuration was LGX263 (100Fe:4.60Si/2.72Cu/0.00K) and as can be seen in Figure

1 (i.e., 'Rewax Flux Density vs Sample Day for Run LGX263') problems were encountered in attempting to remove the rewax for the first 12 sample days. It was found that this inability to remove the rewax during this period was not due to blinding off of the filter, but instead by the line from the reactor head to the rewax trap being heated at a too low of a temperature, specifically lower than the melting point of the reactor product (note that the melting point of the Polywax PW_R3000 is ~130°C at ambient conditions). Once additional heat tracing was applied to the line, rewax removal was then permitted as can be seen for sample days 13-17. The rewax collected during this run showed no visible traces of iron. The next run utilizing the lowered filter was run LGX266 (100Fe:4.60Si/2.72Cu/7.52K) and from Figure 2, the performance of the filter, as measured by flux density (gpm/ft²), can be seen in general to decrease with time. The implication here is perhaps there is increased blinding of the filter with subsequent rewax letdown periods. As in run LGX263, the rewax product was visibly free of iron, and in fact LGX266-005 and LGX266-007 each were tested for iron content and tested at 0.03wt% Fe and 0.01wt% Fe, respectively. Also, note that on this figure there is reference to the Regimesh Filter that has a flux density of 0.13-0.20gpm/ft², surface area of 0.175ft², and a porosity of 18μ (corresponding to ~16 times the area and an increase of 36 times the porosity of the Mott SS-filter that we were using). With the maximum Δp across the Mott SS-filter at 75psid and the Δp across the Regimesh filter not known, there is difficulty in making a comparison of the performance of the filters, but from liquid flow characteristic graphs supplied with the Mott product catalog, if the μ-grade is increased from ½μ to 20 μ (with Δp and viscosity held constant), the flux density (gpm/ft²) increases ~100-fold. However, if the Δp is varied

and the μ -grade and viscosity held constant, there seems to be a linear relationship with flux density.

After the completion of run LGX266, an attempt was made to test out a 2 μ -grade Mott SS-filter, the second of the modifications to improve the re wax removal. This was accomplished by opening up the reactor once it had cooled to 130°C and replacing the ½ μ -filter with a 2 μ -grade filter. Comparing the liquid flow media charts in the Mott catalog for the ½ μ and 2 μ filters, at equal Δp 's and viscosities (for Δp 's of 100, 60, 10, 6, and 1 psid and viscosities of 500, 100, 20, and 5cP's, as well as for water), the average flux density increased by a factor of seven. Once the reactor was back to normal operating conditions, the re wax valve was opened for a re wax letdown period of one hour and unfortunately ~300g of reactor contents were removed. The collected reactor product did in fact have catalyst present, but at the time , it was not known if;

- 1) the wax/catalyst leaked through an improperly tightened filter fitting,
- 2) had it passed straight through the 2 μ -grade filter,
- 3) was due to the fact that the level had dropped so much that the filter was exposed to the gas/froth space that may contain finely ebullated catalyst particles,

or possibly a combination of the above.

Since the 2 μ -grade filter test was inconclusive for run LGX266, after the completion of run LGX268 (100Fe:4.60Al/2.72Cu/3.66K) which also used a ½ μ -filter, another test of the 2 μ -grade filter was attempted. The results from this series of re wax letdowns was more promising in that the re wax product collected appeared catalyst free and thus was justification for the installation of a 2 μ -grade filter prior to the start of a

run. Subsequent iron based catalyst FTS runs have incorporated the use of the 2 μ -grade re wax filter.

The third of the potential solutions to address the problem of re wax removal and reactor overfilling was to develop a mass balance for the system to allow for the prediction of the amount of re wax to be removed so as to maintain a constant reactor inventory. Simply stated,

$$\text{Reactor Accumulation(g)} = \text{Gas}_{\text{in}}(\text{g}) - \text{Gas}_{\text{out}}(\text{g}) - \text{Trap Products}_{\text{out}}(\text{g}).$$

Two versions of this mass balance were developed. The first just accounts for the mass of the gas out based solely on the Carle Series 400 AGC chromatographic data and is referred to the simplified mass balance , while the second, and certainly more sophisticated, utilizes chromatographic data from the HP-5790 as well as the AGC data (this second mass balance was developed by Scott Lambert and is referred to as Scott's mass balance). Both mass balance methods also account for the liquid and solid products out, i.e., water, oil, wax, and re wax. By adding either reactor accumulation terms to the starting weight of the wax/catalyst, a predicted reactor inventory is determined. Figure 3 shows run LGX267 (100Fe:4.60Al/2.72Cu/0.00K) using Scott's mass balance which predicted that there was ~127g remaining in the reactor, while in fact the reactor contents were measured at 92g after the completion of the run. Note that the dashed line across the graph indicates the starting weight of the of the reactor solvent and catalyst in the reactor, which was 318.68g. Figure 4 is for run LGX269 (100Fe:4.60Al/2.72Cu/7.52K), which also had a starting weight of 318.68g. Both the simplified and Scott's mass balances are presented here and up until run hour 144, agree rather well with one another. After run hour 144 there is a divergence of predicted reactor contents in which there is an approximate 50g difference in values. At

the end of the run the disagreement between the two mass balance methods was at ~40g (346g for the simplified and 386 for Scott's), but the actual measured amount of wax/catalyst in the reactor for this run was at 598g, 55% more than what Scott's mass balance predicts and 73% more than the simplified mass balance prediction. These discrepancies have yet to be resolved. Figure 5 shows the results of the two mass balance methods applied to run LGX270 (100Fe:4.60Al/2.72Cu/11.58K). For this run the predicted reactor contents agree to within ~20g of one another (384.8g for the simplified and 363.2g for Scott's method, within 6% of each other), and both prediction models compare well to the final measured wax/catalyst weight of 310g (24% high for the simplified method and 17% high for Scott's method).

Figures 6 and 7 are plots of the 'Net Reactor Accumulation' (i.e., gain/loss from initial starting weight of 344.0g of catalyst/solvent) for runs LGX284 and LGX285', respectively. For run LGX284 (Figure 6), the simplified mass balance was better (95% of the actual/measured value of +408g) at predicting the reactor accumulation than was Scott's mass balance (121% of actual/measured value). The opposite is true for the net reactor gain/loss for run LGX285' (Figure 7). Scott's method predicted a loss of 35g from the starting weight of 344.0g (within 49g of the actual/measured loss of 84g), while the simplified mass balance predicted a gain of 130g. Referring to Figure 7, it can be seen that the two prediction methods agreed with one another to within ~50g, up through run hour 360, but then they diverged to predicting values in disagreement of 165g for the end of the run. It is unclear as to what caused this divergence when they had agreed so well with one another.

The problems concerning the disagreement with the two methods are presently being addressed, as this is potentially a very useful technique for maintaining and

predicting reactor inventory, as well as predicting the amount of re wax to be removed from the reactor on a daily basis.

A fourth solution has been incorporated in attempts to aid in the removal of the re wax product. In the past, re wax letdown was accomplished by opening the re wax letdown valve while closing the wax letdown valve. With the wax valve closed and the re wax filter submerged, there is no discharge path for the gas (unless the reactor's contents are at a level lower than the re wax filter) to exit the reactor and subsequently the reactor pressure climbs. To eliminate excessive increases in reactor pressure, the wax valve would be periodically cracked to vent excess gas in the reactor. This required constant monitoring of reactor pressure and as a result of pressure variations, the FTS reactions were probably affected. With both the wax and the re wax valves open, an exhaust path for the gas is available, as is a path for the removal of reactor product. Although this letdown procedure does not allow for as large of a Δp across the re wax filter as that which occurs when using the former (with wax valve closed), it has been shown that there was sufficient Δp to let down re wax through the filter. Not only was it possible to remove reactor product using this method, but the re wax collected was , visibly clean, which is also a testament to the use of the 2.0 μ -re wax filter. The only difficulties encountered in using this method has been in the prediction of the amount that can be removed over a given period of time.

To enhance the predictability in removing a desired amount of re wax (as determined from the mass balance techniques) a more recent modification of the re wax letdown procedure incorporates the use of Boyle's law to attempt re wax removal. As the re wax sample bomb can be totally isolated from the reactor system without interruption to reactor operation, and the fact that volume of the re wax receiver is known and that the re wax

sample receiver can be independently charged to any pressure, we should be able to predict at what pressure to charge the empty re wax bomb so as to allow for a volume of re wax to be collected. As the re wax is collected, the bomb pressure should increase until it equilibrates to that of the reactor. The verdict is still out on this method of predicting specific amounts of re wax removal, but appears to be promising.

A final method for addressing the problem of reactor re wax removal and that of avoiding reactor overfilling involves the installation of a liquid back flush bomb for the re wax filter. Presently, the re wax bomb itself can be used as a gas charging vessel by isolating the bomb by closing the re wax letdown valve and the equalizing valve between the re wax and wax traps. An inert gas can then be introduced into the re wax bomb at a pressure higher than that of the reactor and the re wax valve can then be opened and the gas pressure can force the hydraulic column of re wax (contained in the re wax line and the re wax filter) to back flush the filter. Although this capability does exist, it is felt that there is simply not enough re wax present in the line and filter to perform an adequate backflush as well as the fact that the re wax letdown valve is of the flow control/throttling type of valve and does not allow for an instantaneous surge of higher pressure gas to back flush the re wax material such as a ball valve would offer. With a bomb installed on the branch of a tee (with a ball valve separating the bomb and the branch of the tee) and the run of the tee plumbed between the reactor head re wax discharge port and the existing re wax valve, liquids such as C-30 oil could be used to facilitate this back flush.

The importance of cleaning the filter cannot be understated, and can be demonstrated by returning to Figure 2 of Section 3.3.7.6, where it is seen that as time progresses, the flux density decreases, requiring longer periods of letdown time to

remove the desired amounts of re wax, which are determined by using either of the reactor mass balance techniques.

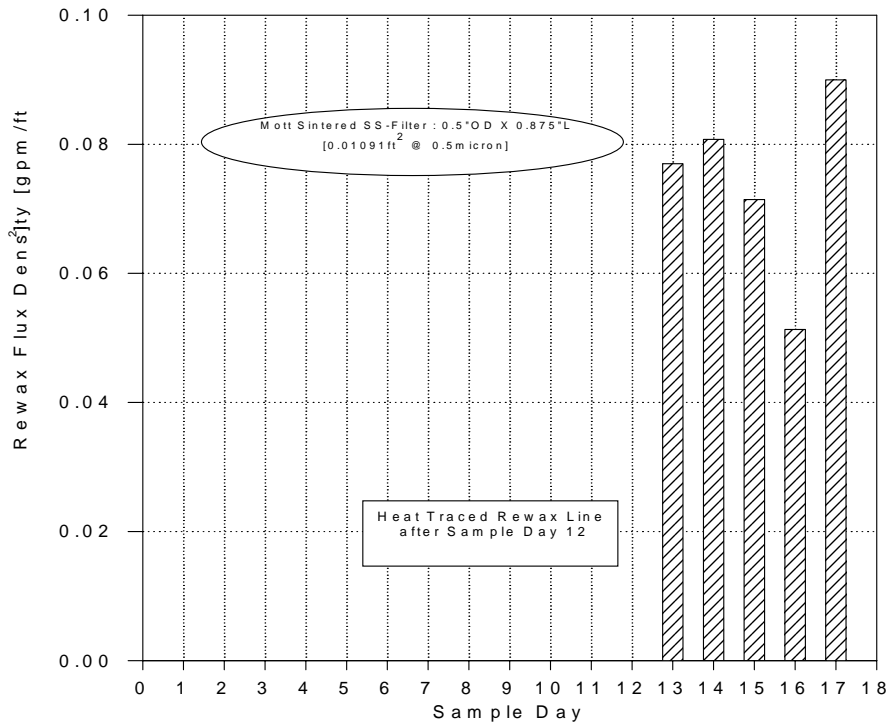


Figure 1. Rewax Flux Density vs Sample Day for Run LGX263_{R7}.

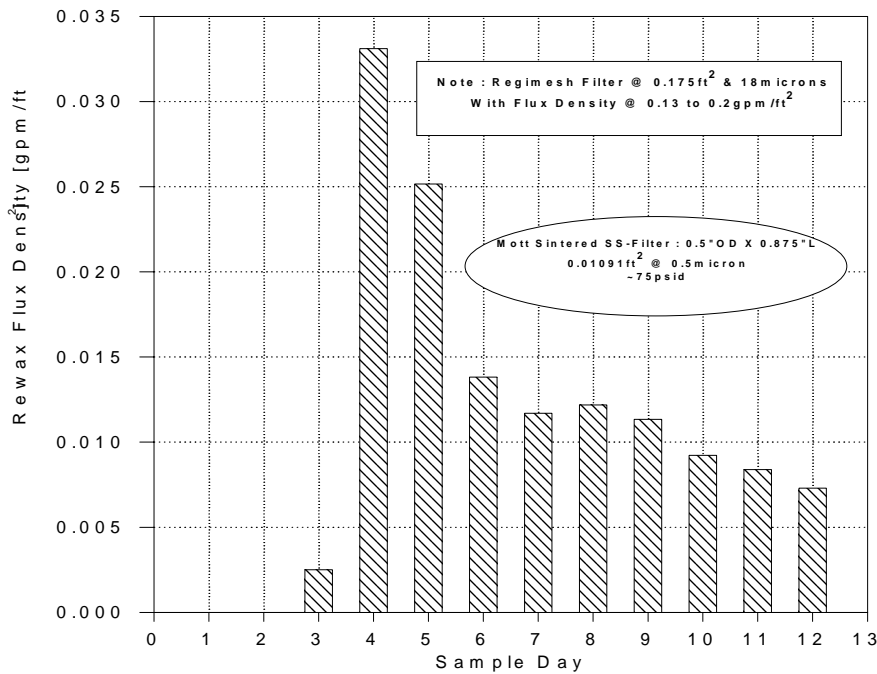


Figure 2. Rewax Flux Density vs Sample Day for Run LGX266_{R7}.

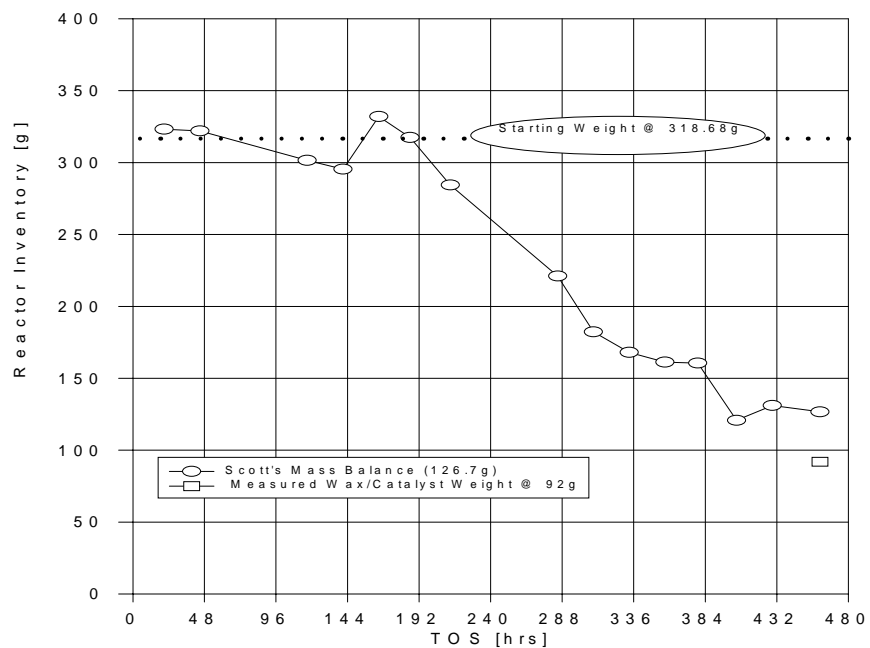


Figure 3. Predicted Reactor Inventory vs Time on Stream for RunLGX267_{R1}.

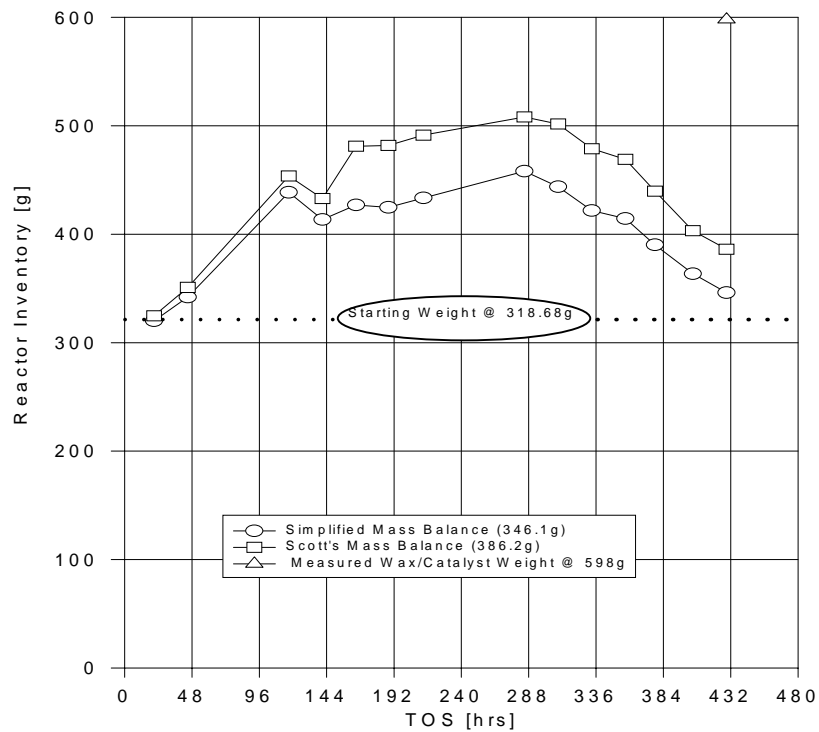


Figure 4. Predicted Reactor Inventory vs Time on Stream for RunLGX269_{R3}.

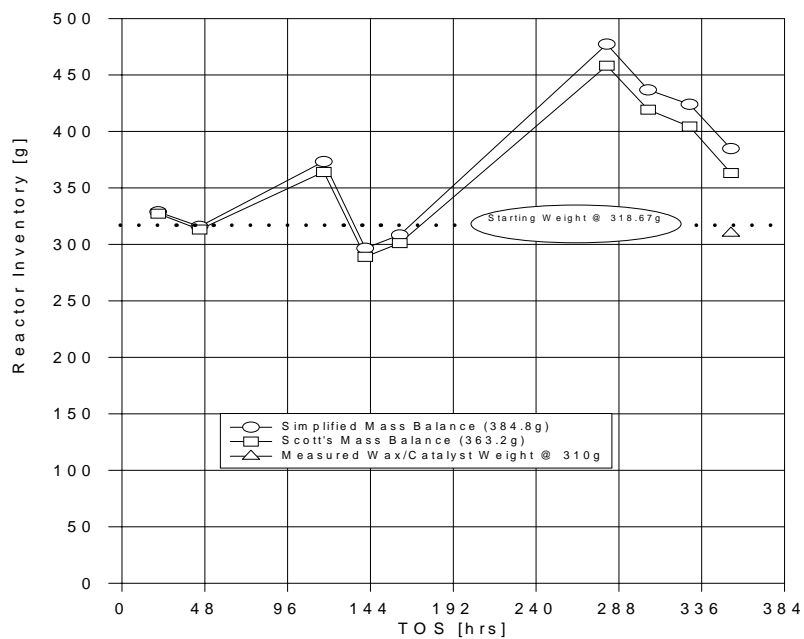


Figure 5. Predicted Reactor Inventory vs Time on Stream for Run LGX270_{R4}.

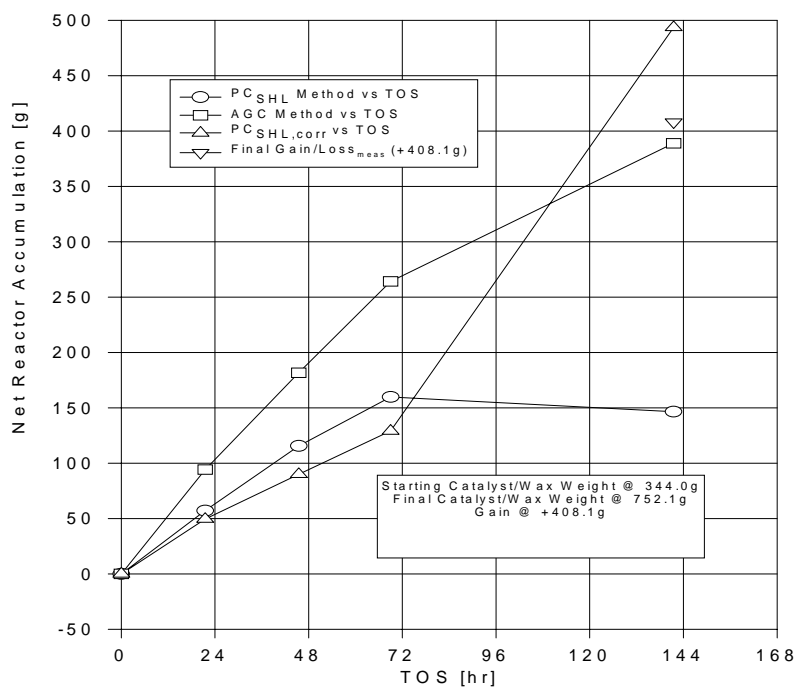


Figure 6. Net Reactor Accumulation vs Time on Stream for Run LGX284.

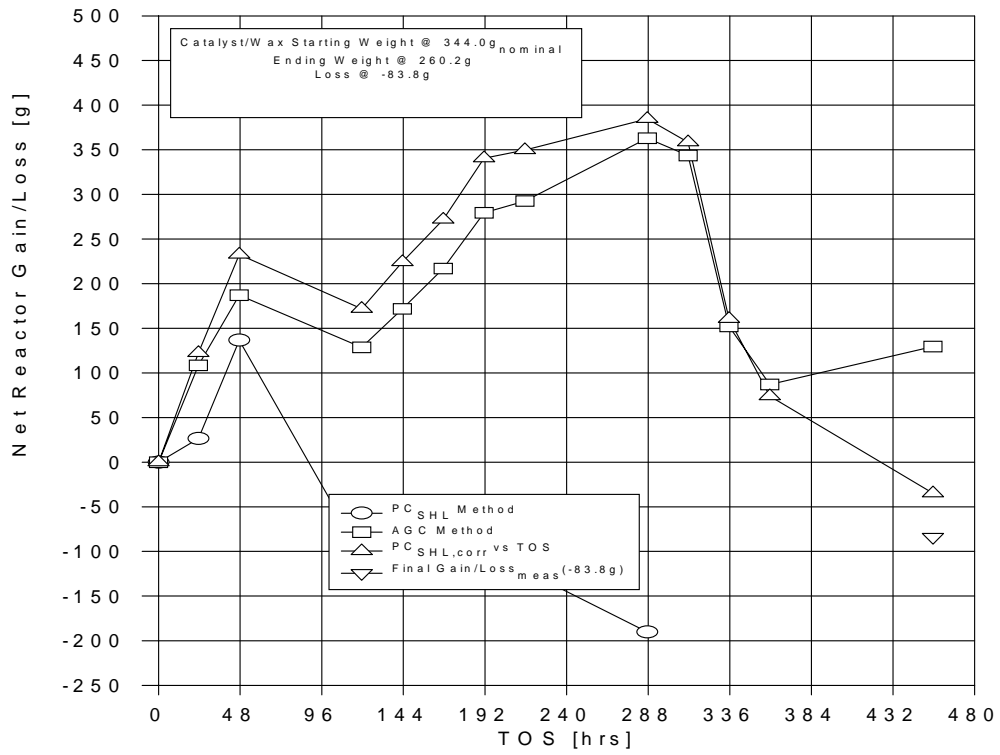


Figure 7. Net Reactor Accumulation vs Time on Stream for Run LGX285'.