8. J. A. Amelse, L. H. Schwartz, and J. B. Butt, *J. Catal*., **72** (1981) 95.

9. D. Bianchi, S. Borcar, F. Toule-Gay, and C. O. Benett, *J. Catal*, **82** (1983) 442.

10. G. L. Vogler, X. Z. Jiang, J. A. Dumesic, and R. J. Madon, *J. Catal*., **89** (1984) 116.

11. E. Murad, and J. H. Johnson, in "Mossbauer spectroscopy applied to inorganic chemistry", Plenum Press, New York, NY, 1987, Vol. 2, pp 512.

Task 4. Wax/Catalyst Separation

The objective of this task is to develop techniques for the separation of catalysts from FT reactor slurries.

4.1. Initial Filtering Studies with Pall Corporation Filters

Summary of Separation Work

Wax separation from a catalyst slurry for slurry bubble column reactor operation can be viewed from two perspectives:

12. Separation of wax from large (50-100 micron) sized catalyst particles formed by spray drying and made attrition resistant.

13. Separation from small catalyst particles (1-3 micron) and eliminate the need for attrition resistant large particles.

The immediate separation problem to be solved by CAER work is to be able to operate a laboratory reactor to define activity, selectivity and aging characteristics of high alpha iron catalysts. A longer term solution is to develop procedure for the operation of the LaPorte facility and potential commercial operation.

The CAER efforts apply for two catalyst systems: cobalt and iron.

Cobalt Catalysts

CAER personnel have prepared supported cobalt catalysts based on alumina, silica and titania support material. The supports have sufficient attrition resistance to retain their physical shape and size during weeks of operation in a CSTR.

CAER personnel have successfully removed wax from the reactor during operations of up to five months using supported cobalt catalysts. The only wax separation problem with cobalt catalysts was when testing for a company (work outside DOE contract) due to attrition of a poor support.

Conclusion

Wax separations from catalyst slurry is not a problem using a fine (2 to 5 micron) porous metal filter. Operations of laboratory reactions with wax production of 100g/day or higher can be accomplished. Wax removal is therefore not a problem with supported cobalt catalysts in the laboratory setting. For Run 4 at LaPorte, it has been reported that filtration was not a problem but was a problem for Run 3 with a similar catalyst.

Iron Catalysts

All spray dried iron catalysts that have been tested at CAER have attrited to 1-3 micron sized particles during the activation period. Supported iron catalysts can be utilized without attrition of the support.

Using a porous metal filter with the small (1-3 micron) sized iron catalyst, operates with a 10 wt.% slurry of a high-alpha unsupported iron catalyst had to be terminated after 200-400 hours due to filter plugging, resulting in the reactor filling with wax. With the supported high-alpha iron catalysts, the support did not attrite but the filter plugged; it is assumed that this was due to the small iron particles being released from the support.

Wax removal has now been accomplished when the small (1-3 micron) high-alpha (0.92) iron catalysts are used in a laboratory reactor containing 10 wt.% slurry. A Rigimesh filter permitted operation for 1450 hours (2 months) without having the filter plug. When the run was voluntarily terminated, the filtration rate had not declined. The run was terminated in order to make a run that contained a higher wt.% catalyst slurry. Using the same catalyst with finer pore openings resulted in filter plugging after 100 hours (very fine filter) and 1000 hours (medium porosity filter). Using the Rigimesh filter, the catalyst loss with the withdrawn wax was about 1%/week; the catalyst activity also declined at about 1%/week.

Conclusion

The Rigimesh filter can be utilized to permit the operation of the laboratory reactor to define the long-term activity and selectivity of intermediate and high-alpha iron catalysts. The wax removal flux is lower than desired for commercial operation; however, the rate obtained during the CAER initial work should be viewed as the minimum. Should this initial success continue, we will be able to operate laboratory reactors without the need to develop attrition resistant iron catalysts.

Detailed Description of Filtration Study with Pall Filter

Two filters manufactured by Pall Corporation were installed in 1000 mL continuous stirred tank reactors. The filters had the same geometrical external surface area as the Mott Metallurgical sintered filters used previously. Two types of filtering media were used. One filter used a material called Rigimesh (filter A). Rigimesh is a sintered woven wire mesh which Pall Corp. reports as having the greatest permeability for comparable removal efficiency. Sintering increases the strength of the mesh by bonding the wire at each point of contact which prevents shifting of the wires and maintains a constant pore size. The filter used in this study was a

multilayer composite of different mesh sizes. The other filter tested is composed of PMM medium (filter B). PMM medium is a thin sintered matrix of stainless steel powder within the pores of sintered stainless steel mesh. The sintered powder allows for filtration down to μm and the stainless steel mesh provides strength.

Each filter was tested with the same high alpha catalyst. The catalyst was prepared by standard continuous precipitation techniques and impregnated with KNO_3 and $Cu(NO_3)_2 \cdot 3H_2O$ to give an atomic composition of 100Fe/4.6Si/2.0Cu/5.0K. The reactor was loaded with 32.2 g of catalyst and 310 g of decene trimer. The catalyst was activated with CO at 270°C, 175 psig for 24 hours. Following activation, syngas ($H_2/CO = 0.67$) was started at a space velocity of 3.1 sl h^{-1} g-Fe^{-1}. The temperature and pressure were maintained at 230°C and 175 psig, respectively.

A schematic of the reactor, traps and filtering system is shown in Figure 1. Reactor effluent (vapor phase) exited through valve 1 which was open at all times, unless the filters were being purged. Valve 2 was normally closed. Wax removal was accomplished by venting the wax trap to 125 psig (50 psi less than reactor pressure) with valve 3 closed (wax trap isolated from reactor and 60°C trap) followed by slowly opening valve 3. Wax removal was considered to be finished when the pressure of the wax trap was equal to the reactor pressure. Accumulated reactor wax was removed approximately every 24 hours. The first wax samples appeared black due to catalyst penetrating the filters. After a few days the wax samples appeared clean, presumably due to the formation of a filter cake on the filter. The amount of wax removed during the first 5 minutes that valve 3 was open was determined on most days to calculate the rate of filtration and determine if the filters were plugging. The initial filtration rates for the two types of filters are shown in Figure 2. The filtration rate of the PMM filter was higher than the Rigimesh filter for the first 380 hours. It is emphasized that these are minimum filtration rates.

The reactor plumbing was arranged such that the filter could be periodically purged with Ar in order to clean the filtering medium and prolong filter life. To purge the filter, valves 1, 2 and 3 were closed. Valve 4 was opened to pressurize the wax trap with Ar up to 250 to 400 psig. Valve 3 was opened slowly to allow Ar to flow back into the reactor through the filter. The first time the filter back purge was done was at approximately 390 hours of the run with the Rigimesh filter. The filter was purged with 300 psig Ar and showed no signs of plugging because the reactor pressure rose immediately and within seconds the wax trap and reactor pressures were identical. A wax sample was taken 30 minutes after purging the filter and it appeared black due to catalyst penetrating the filter (just like the wax samples at the beginning of the run). Twenty-four hours after purging the filter the wax withdrawn through the filter appeared clean. Once again, the clean wax was probably due to better filtration from the build-up of a cake on the filter. The PMM filter was also purged after approximately 510 hours on stream. This filter seemed to be partially plugged because it needed to be purged 6 times with Ar pressure ranging from 250 to 400 psig; however, it was successfully cleaned by the back purges. The cumulative wax yield for each run is shown in Figures 3-5. The cumulative wax yield was the same for each run and after 700 hours, and about 1.4 kg of wax had been removed from each reactor (Figure 3).

Syngas conversion as a function of time on stream is shown in Figure 6 for both runs. The conversion was nearly superimposable for the two runs, indicating excellent reproducibility of catalyst activation and activity measurements. There was an induction period of about 3-5 days in which the conversion increased from about 17% to 49%. After the conversion peaked, the catalysts deactivated at the rate of 3.4% syngas conversion (absolute, not relative) per week. Methane selectivity for the two runs decreased to below 2% after 100 hours (Figure 7) on stream which is indicative of high alpha catalysts (alpha-2 was 0.92 for both catalysts).

These runs represent the first time that a high loading of precipitated iron catalyst was run at the CAER under high alpha conditions with 10 wt.% slurry for an extended time (> 800 h). Typically with the Mott Metallurgical filters, high alpha runs were terminated after approximately one week due to filter plugging and subsequent filling of the reactor with wax.

The cumulative iron in the products from run BAO 36 (using the filter A) and BAO 35 (using filter B) are shown in Figures 8 and 9, respectively. During the period up to about 150 hours very little reactor wax was removed as the reactor filled to the filter level. For the period of about 150 to 200 hours the first significant reactor wax was removed from the reactor (Figure 4). During this same period a significant amount of iron (about 1 g) was removed using filter A (Figure 8). This is a clear demonstration of iron leakage through the filter during the initial wax withdrawal period. From the period of about 200 to 390 hours on stream, the removal of iron was slower and at a nearly constant rate of about 0.22 g Fe/week. At run hour 390 the filter was backflushed using argon. After the backflushing, there was a period of rapid iron removal (about 0.4 g Fe in one day). This conclusively shows that the backflush was effective in partially, or completely, cleaning the "cake" of iron deposited on the filter. Following this backflush, the filter was operated without backflushing. From 400 to 1,000 hours on stream the iron and reactor wax was removed at a constant rate. During this 600 hour period, the slope of the line in Figure 8 indicates that iron was removed at a rate of 0.18 g Fe/week. The values of 0.22 and 0.18 g Fe/week for the two periods of constant iron removal are in excellent agreement considering the length of time for the run. Since the reactor was loaded with 20 g of iron, the filter permitted the passage of about one percent per week of the iron. The run was terminated after almost 1500 hours (2 months) of continuous operation. The filter was operating as well at the end of the run as it was during the course of the run. The termination with this filter was voluntary, and not due

to filter plugging. **Thus, we consider this to be a demonstration of our ability to operate the CSTR so that we can now define the activity, selectivity and catalyst deactivation characteristics for both the intermediate and high alpha catalyst.**

The run (BAO 35) using filter B was less effective that for filter A. The run had to be terminated after about 1,000 hours on stream due to the filter plugging. This allowed the reactor to fill with reactor wax. This filter has been sent to be cleaned by a commercial organization recommended by Pall to learn whether it can be reused after cleansing or whether the plugging is so severe that the filter must be discarded. Filter B has a component that has finer openings that filter A; thus, it is assumed that the plugging is due to the finer average pore opening.

The alkali content of the high-alpha, low-temperature catalyst has a significant impact upon the conversion that is attained. The alkali content of the catalyst utilized in these two runs was about 5 wt%, and this is below the level that should give the maximum conversion. Even so, the conversion is in the range of 30-45% and the hydrocarbon productivity rate is 0.22-0.35 g hydrocarbon/g Fe/hr. This productivity rate compares favorably with those reported for the productivity of cobalt catalysts when the cobalt productivity is based on g hydrocarbon/g catalyst/hr). Early indications are that the catalyst formulation with 7.5 wt.% potassium has about twice the productivity of the catalyst containing 5 wt% potassium.

There is a reasonably long induction period in which the activity increases, then attains a maximum which is followed by a period where the activity gradually declines to a nearly constant activity after about 500 hours on stream. During the period between 800 and 1463 hours, the activity declines at a rate of 0.8% CO conversion/week. During this period the iron catalyst in the reactor is declining at a rate of about 1%/week. **Thus, the activity decline is at**

approximately at the same rate as the loss of catalyst, and the catalyst activity decline is clearly lower that the DOE target of 1% CO conversion/week.

The catalyst with 5 wt% potassium is a high-alpha catalyst with the second alpha being about 0.92. The methane make is consistent with a high alpha catalyst and is about 1.5 wt% of the total hydrocarbon fraction (Figure 7). The fraction of the C_2 fraction (Figure 10) that is represented by ethylene (about 85%) is representative of a high-alpha catalyst, as is the C_3 (Figure 11) and C_4 (Figure 12) olefin fractions. The fraction of CO converted by the water-gas-shift reaction is about 0.35; thus, about 65% of the CO that is converted is to hydrocarbons.

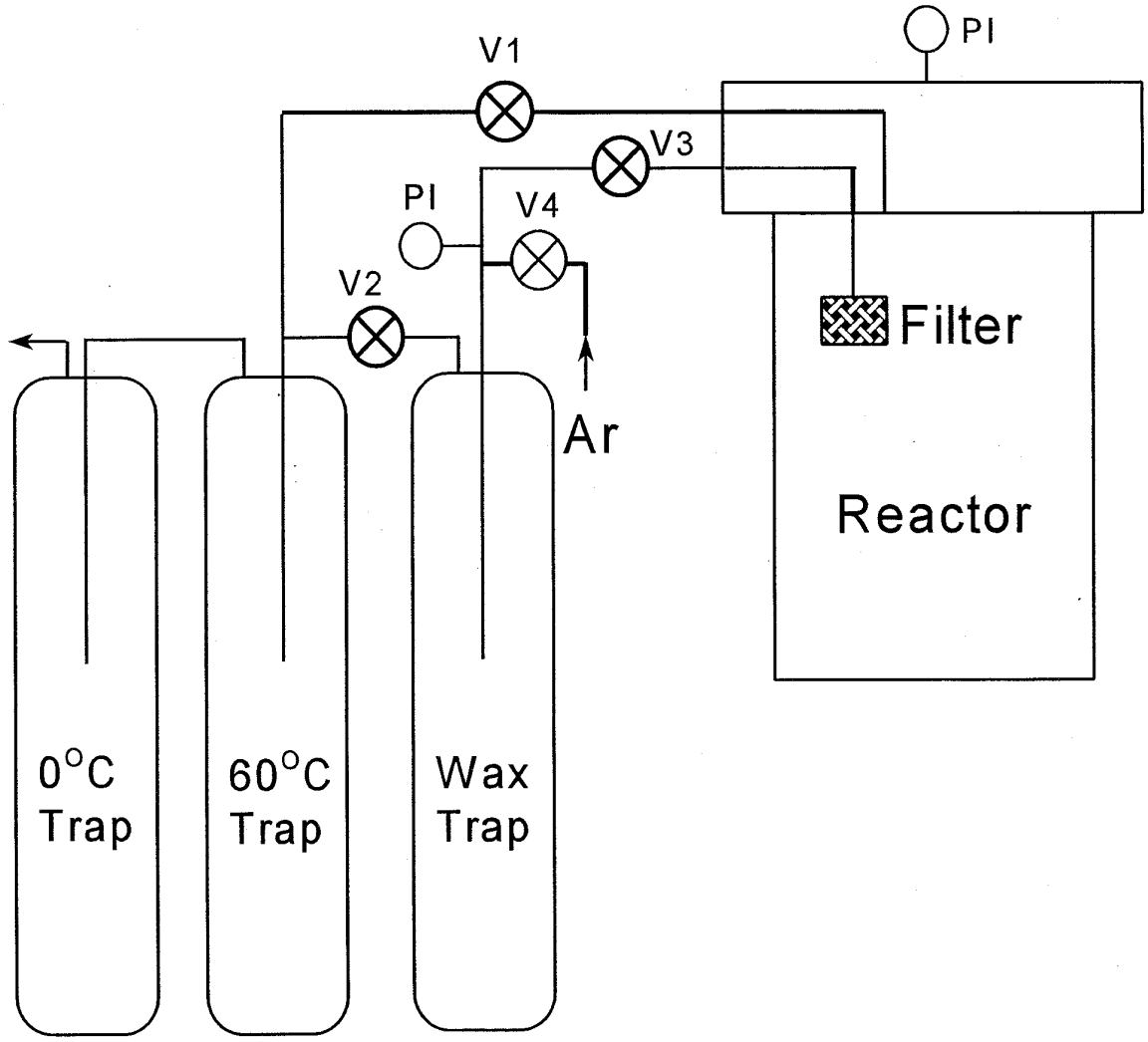

Figure 1.

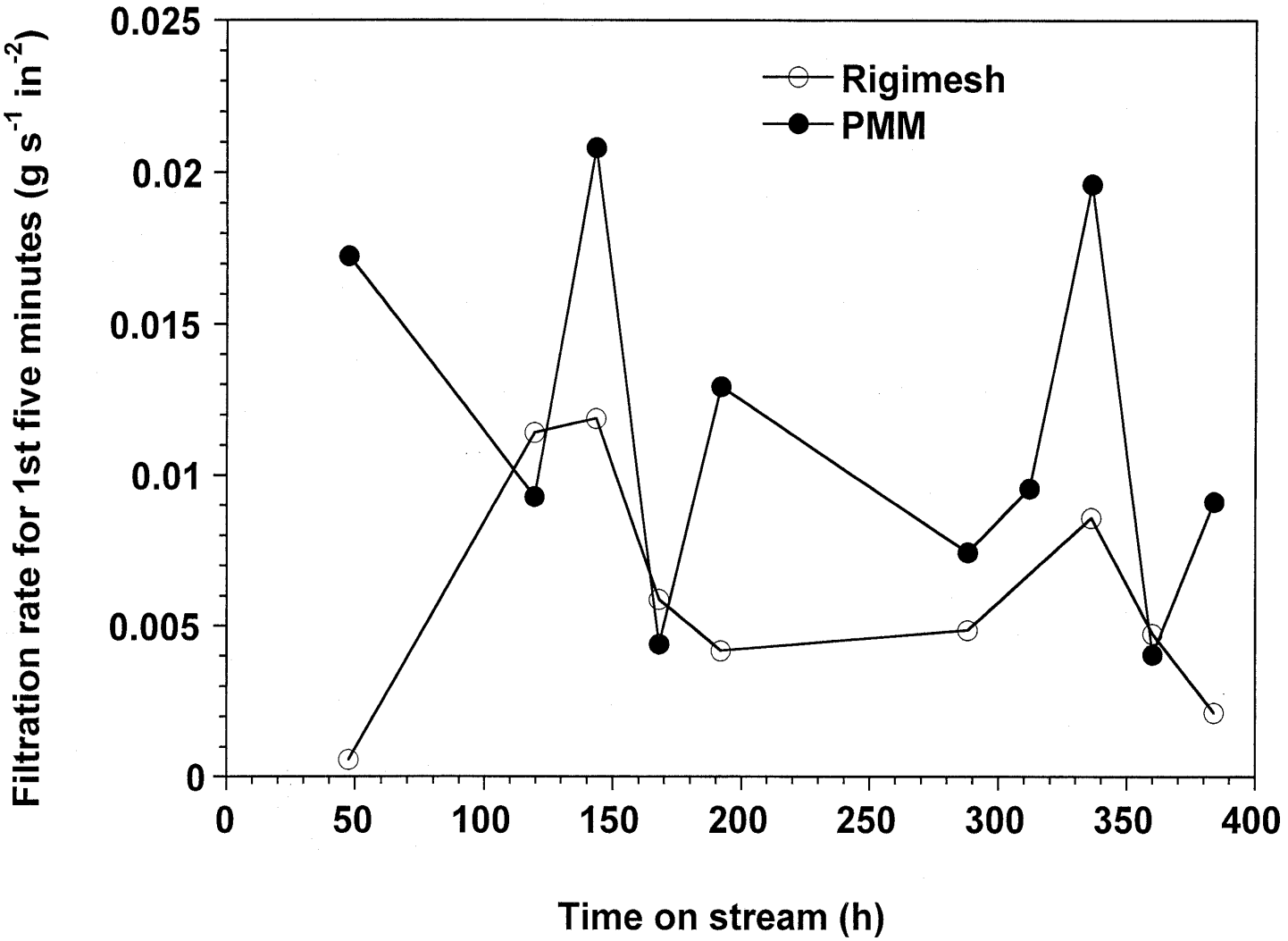
Filtration rate for 1st five minutes (g s-1 in-2)
0.025
0.02
0.015
0.01
0.005
0
0
50
100
150
200
250
300
350
400
Time on stream (h)
Rigimesh
PMM

Figure 2.

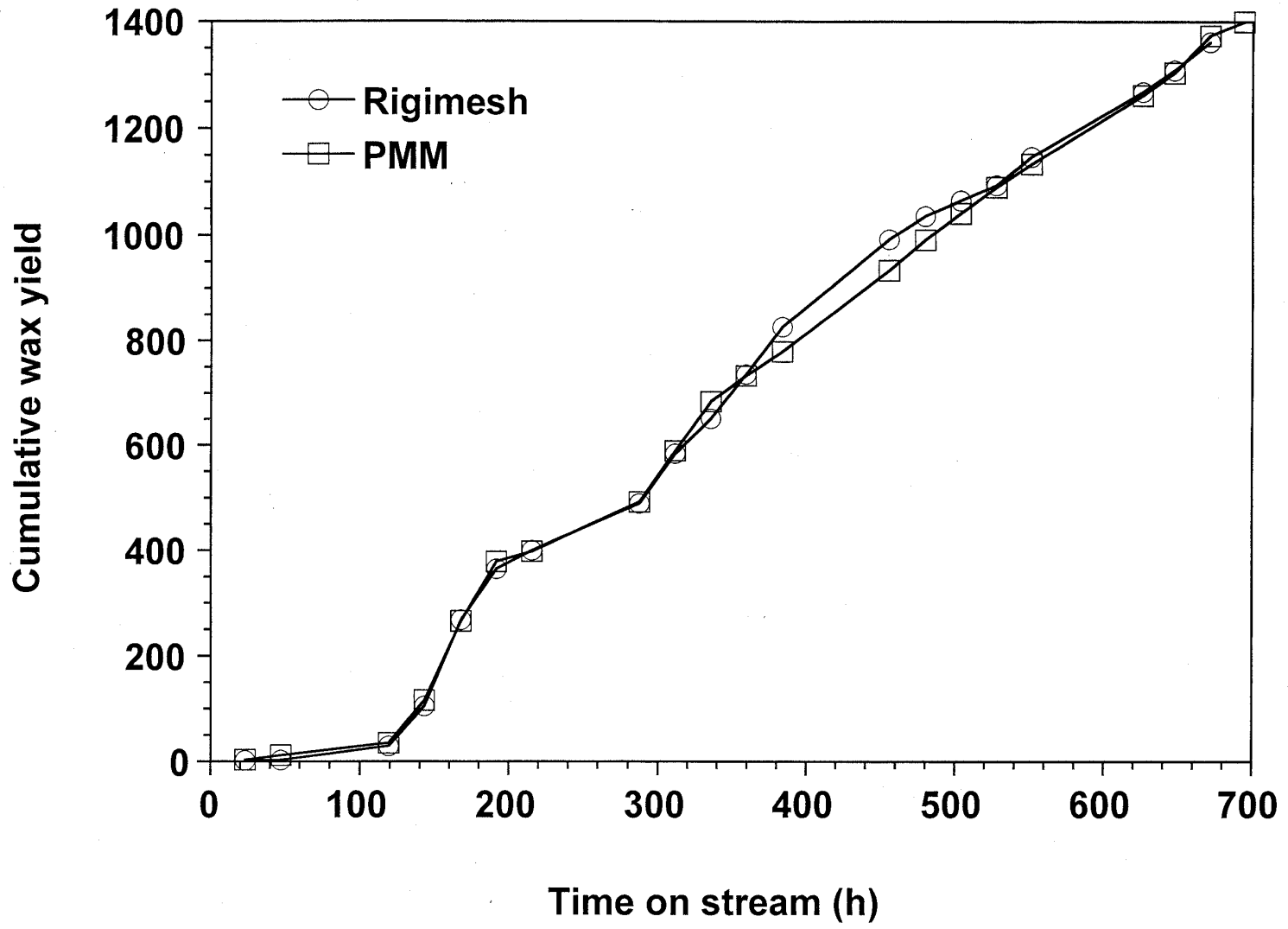
Rigimesh
PMM
Cumulative wax yield
Time on stream (h)
0
200
400
600
800
1000
1200
1400
0
100
200
300
400
500
600
700

Figure 3.

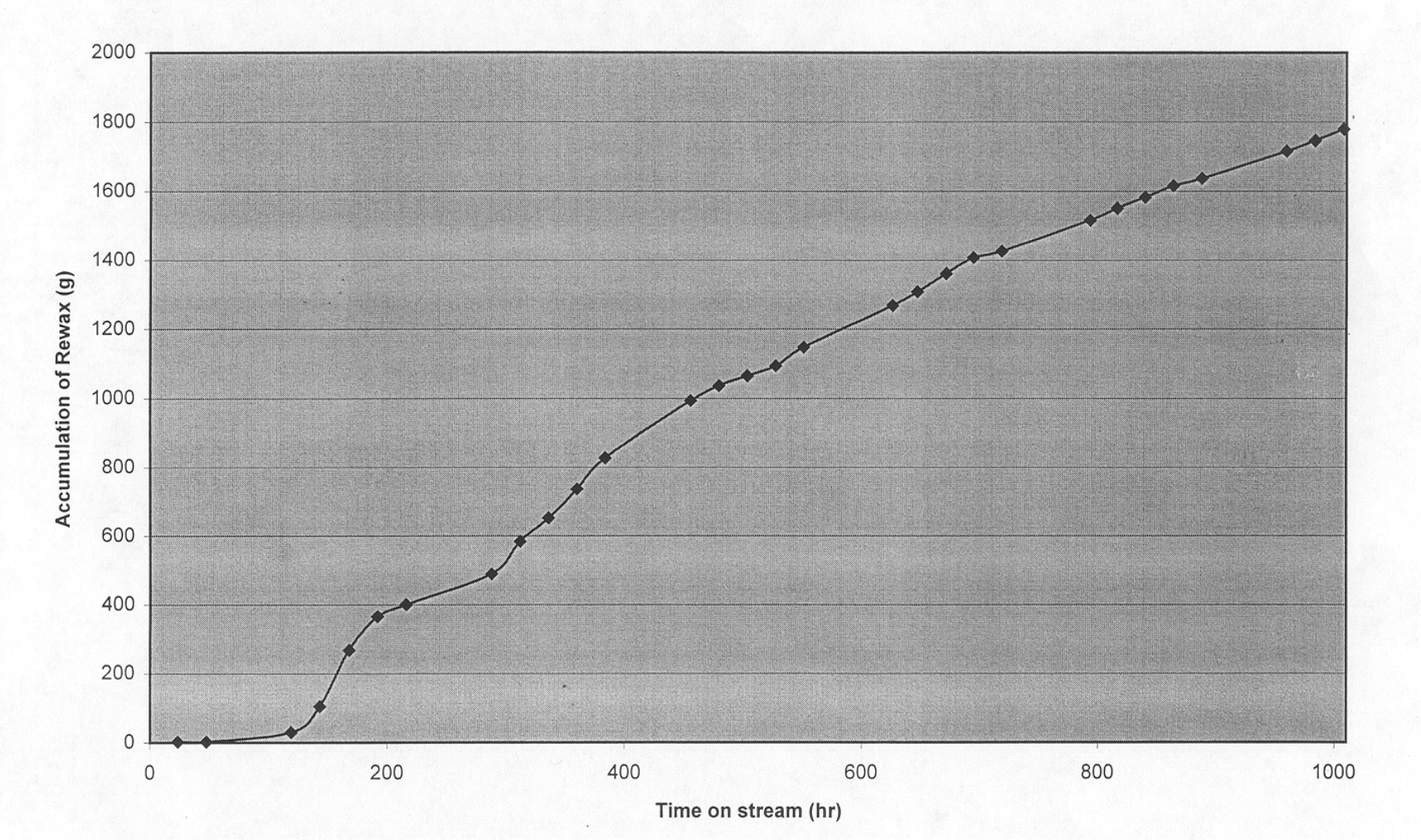

Figure 4. Accumulation of rewax vs. time on stream for filter A.

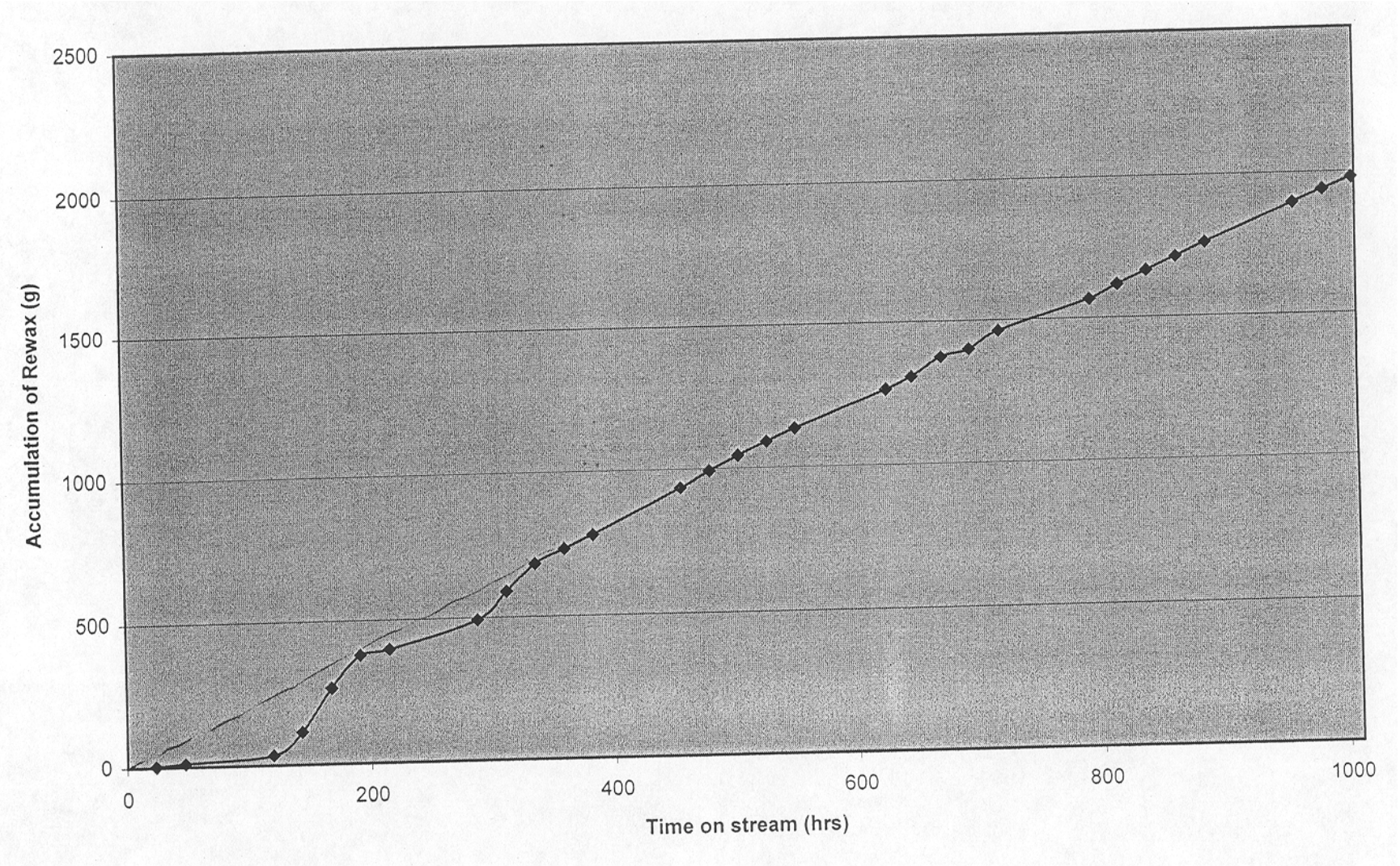

Figure 5. Accumulation of rewax vs. time on stream.

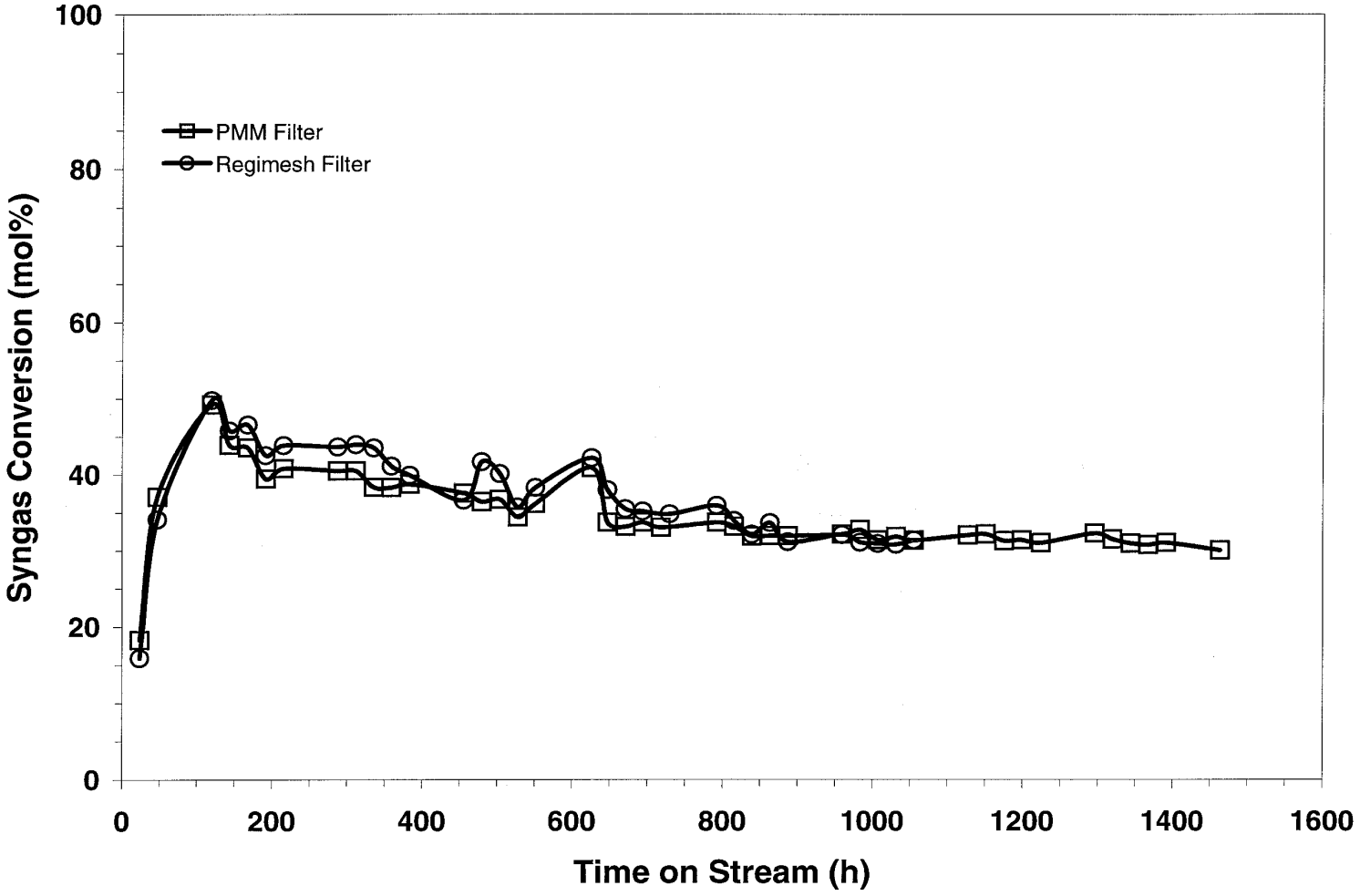
100
80
60
40
20
0
Syngas Conversion (mol%)
PMM Filter
Regimesh Filter
0
200
400
600
800
1000
1200
1400
1600
Time on Stream (h)

Figure 6.

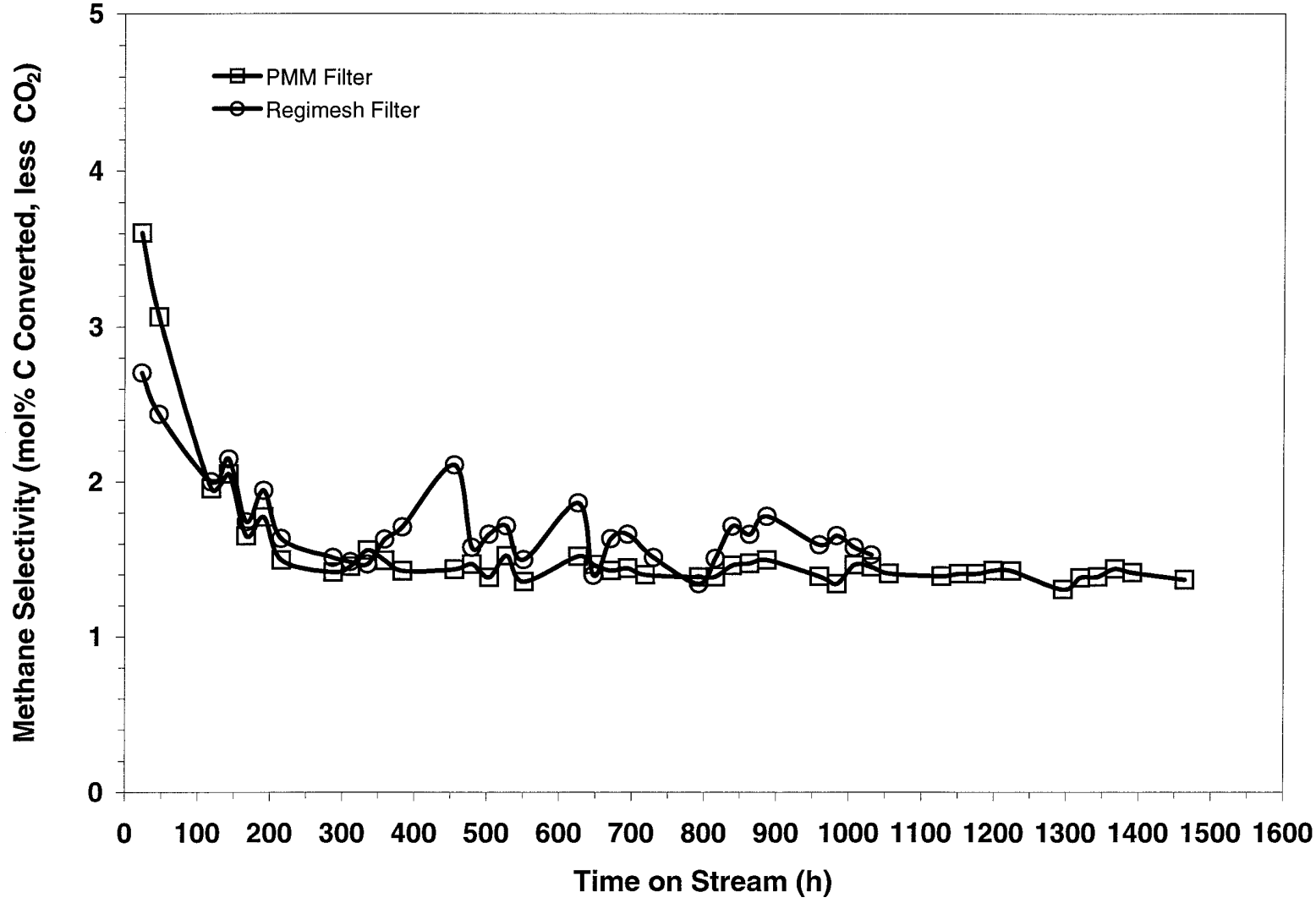
PMM Filter
Regimesh Filter
Methane Selectivity (mol% C Converted, less CO_2)
Time on Stream (h)
0
1
2
3
4
5
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600

Figure 7.

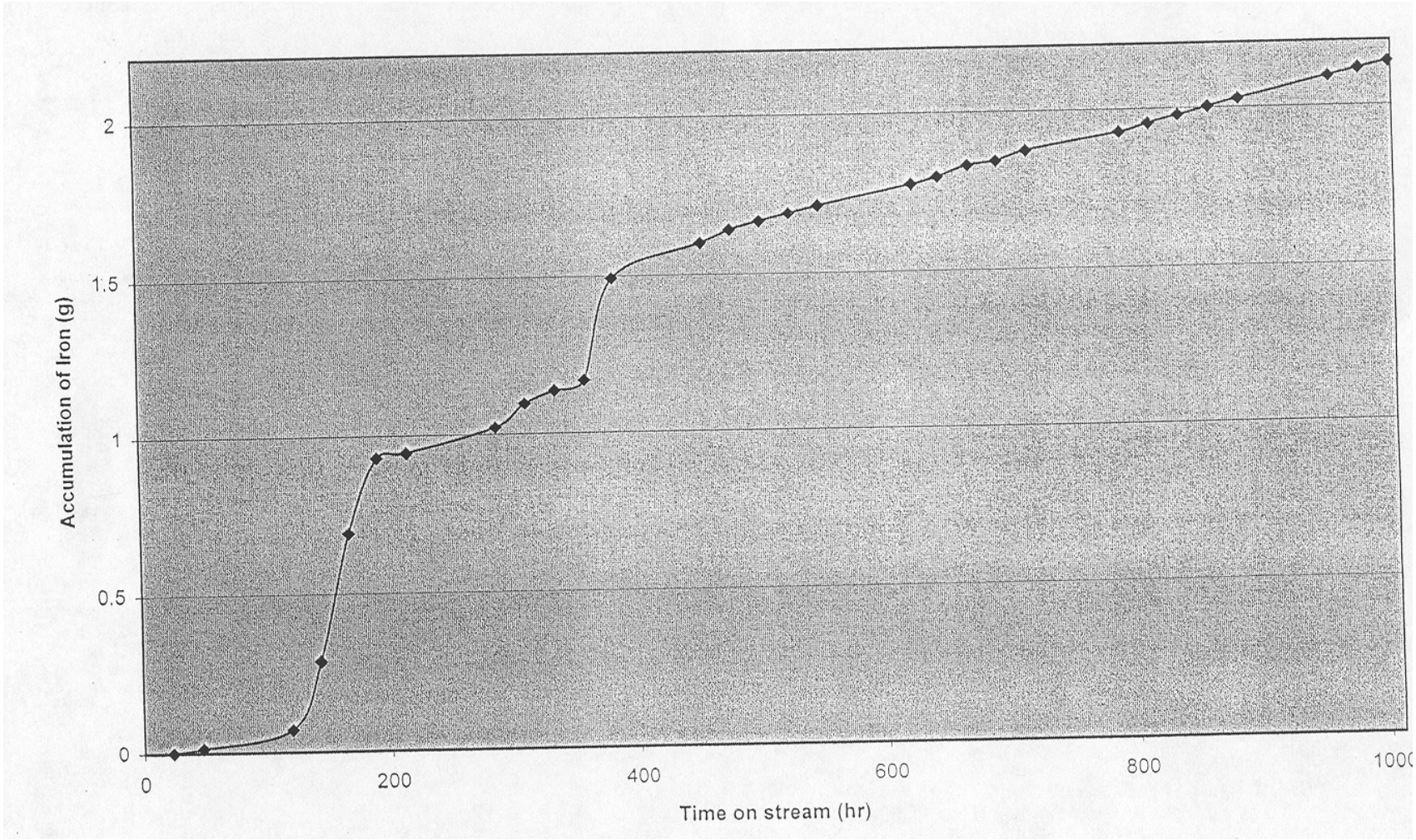

Figure 8. Accumulation of iron vs. tine on stream.

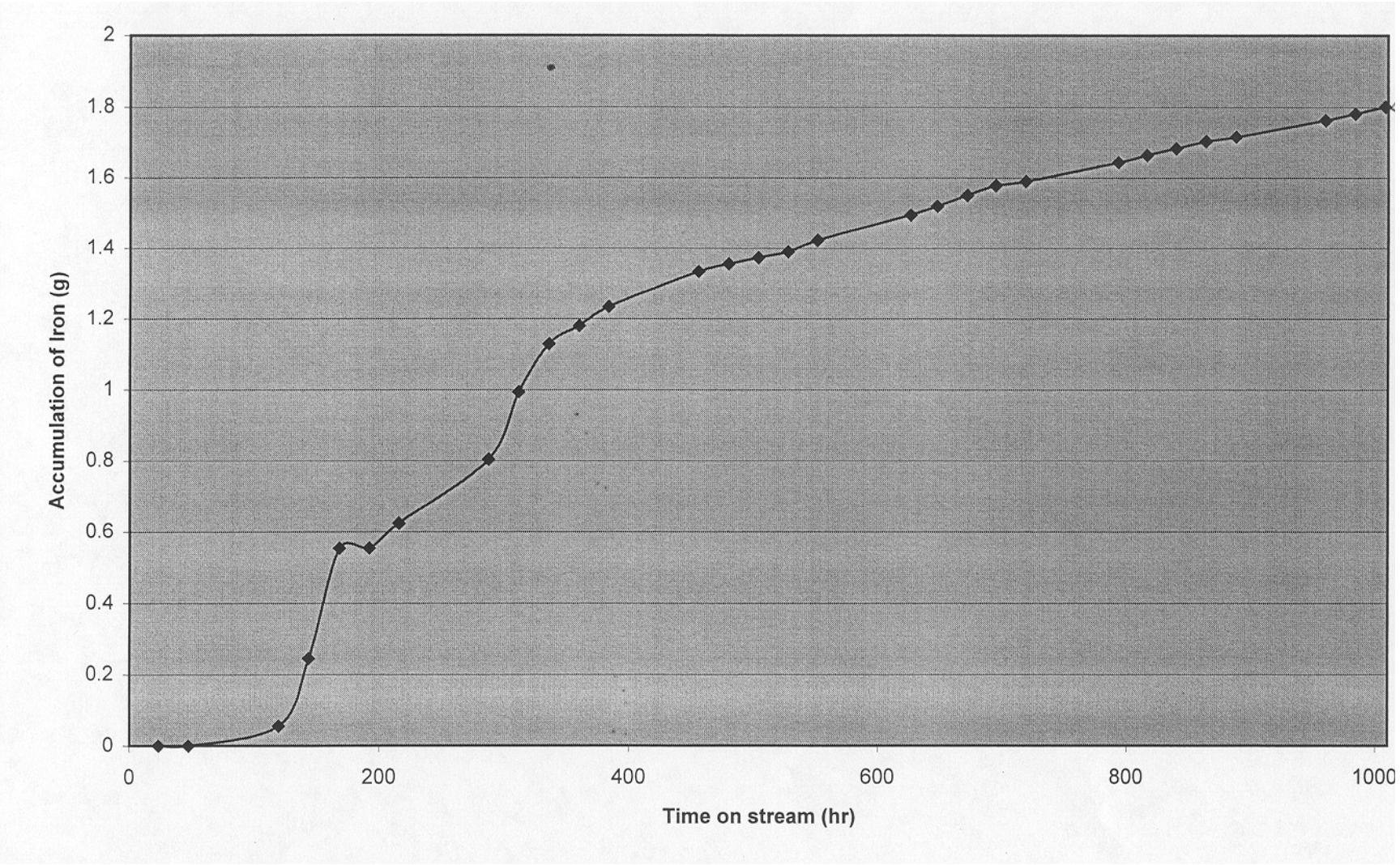

Figure 9. Accumulation of iron vs. time on stream.

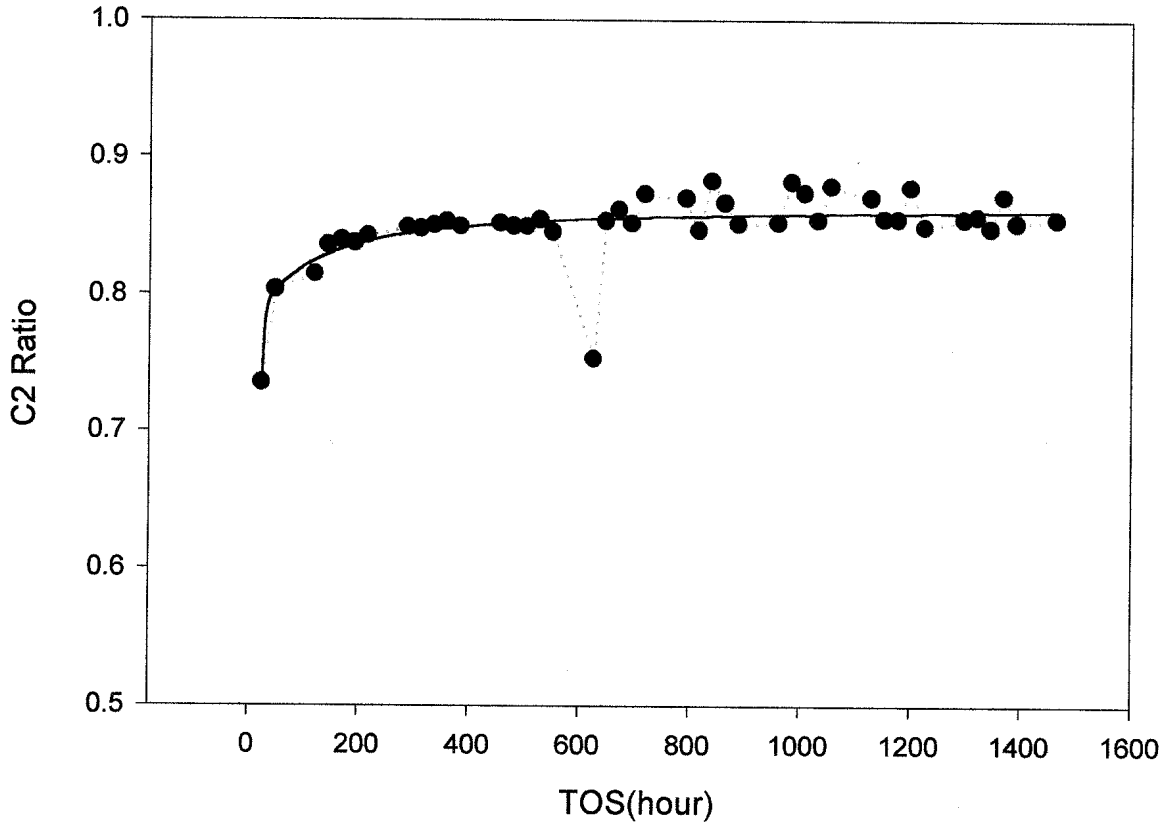

Figure 10. C_2 ratio vs. time on stream.

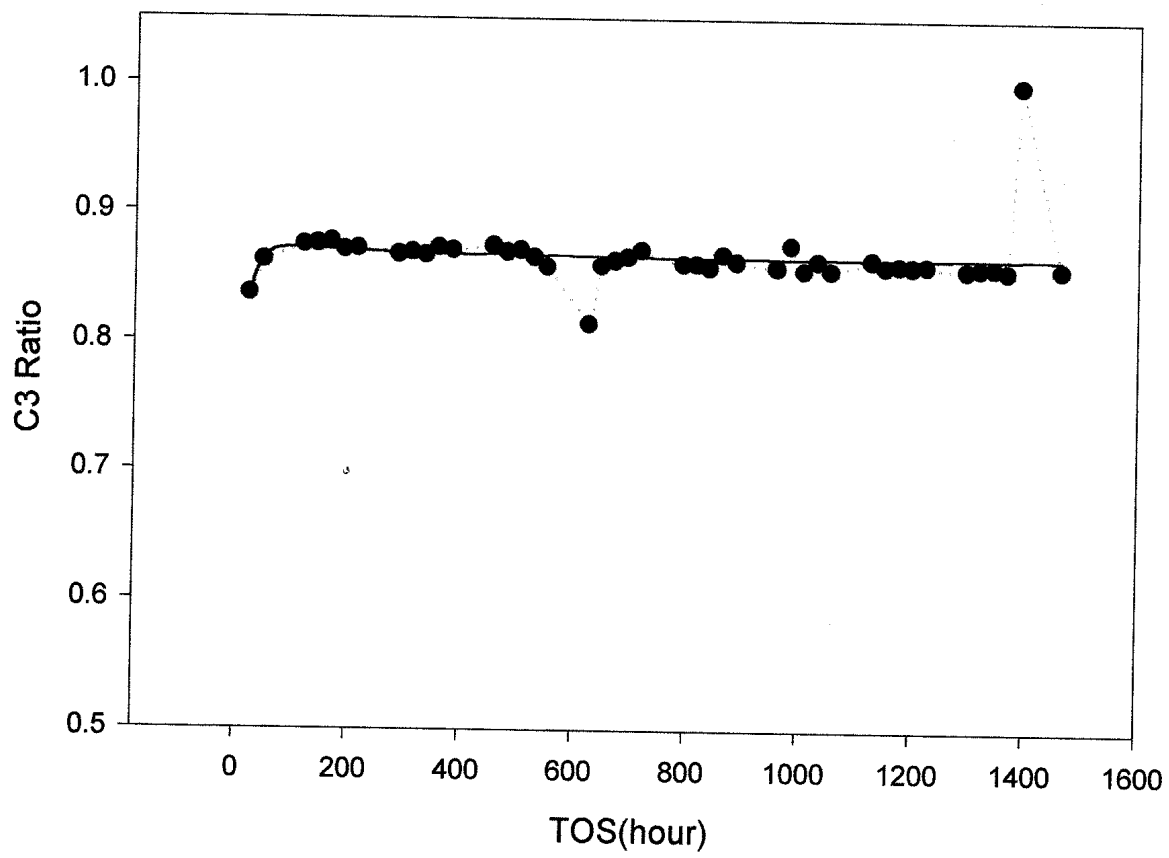

Figure 11. C_3 ratio vs. time on stream.

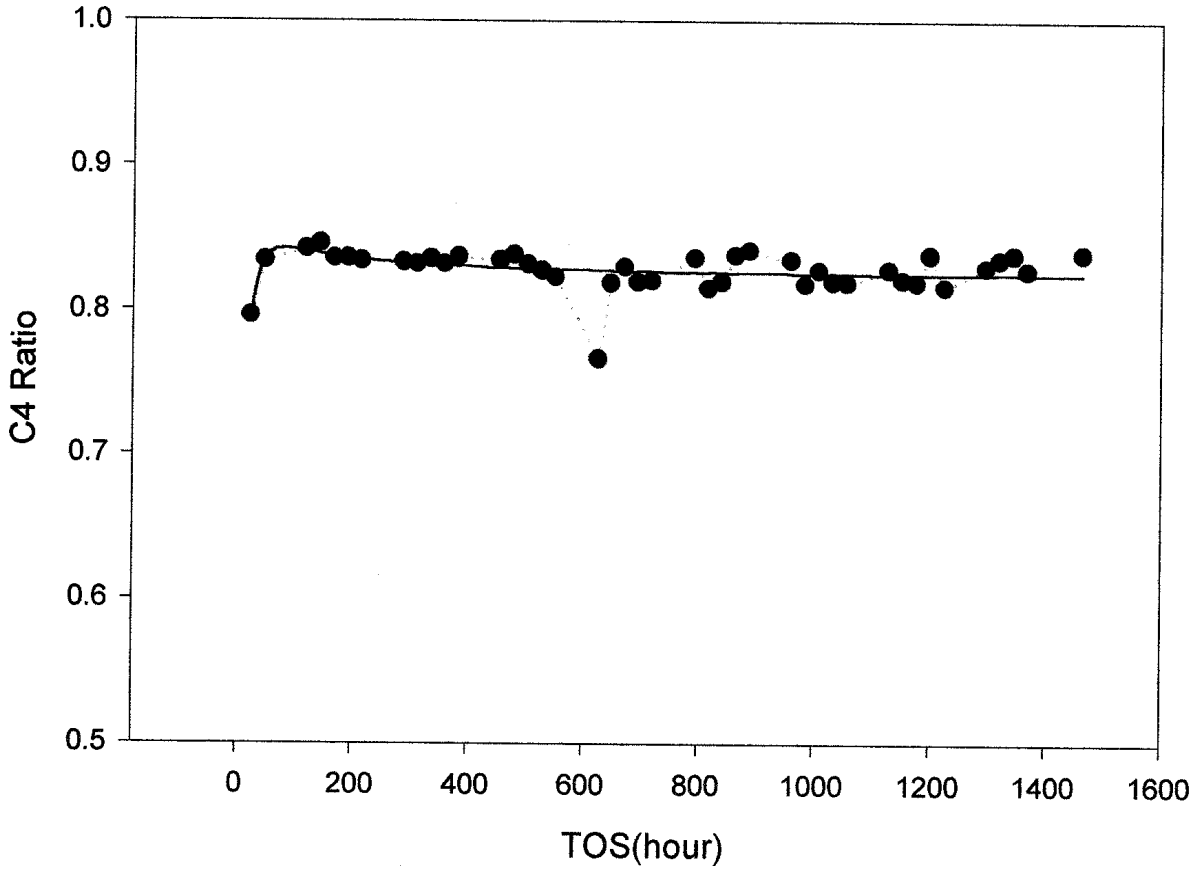

Figure 12. C_4 ratio vs. time on stream.