Fixed Bed Hydrogenation of Proprietary Oleochemical Derivative

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Overview

A fixed bed continuous hydrogenation show-tube pilot unit has been used to produce a hydrogenated Oleochemical derivative with 97-99% conversion to hydrogenated product in a single reactor pass. The fixed bed continuous hydrogenation process was done using a 10' reactor bed containing a Palladium based activated carbon monolith catalyst (ACMC-Pd-100-101C) in up-flow mode. The production run conditions used to make 2000 lb of product with 98% +/- 1.0% selectivity to the hydrogenated product was achieved using run conditions of 220 °C shell temperature, 300 psi pressure and an LHSV of 0.21 hr^{-1}. The catalyst showed no evidence of deactivation after a run time of 1000 hours. From this work, an initial reactor size can be linearly scaled by adding more reactor tubes. For example, to produce 4 tons of product per day (~ 3 million lbs/year), a reactor comprised of 364 tubes (10 ft catalyst bed length, 1.18" I.D.) would be required. This reactor would have a shell diameter of 2.5 ft. [1]

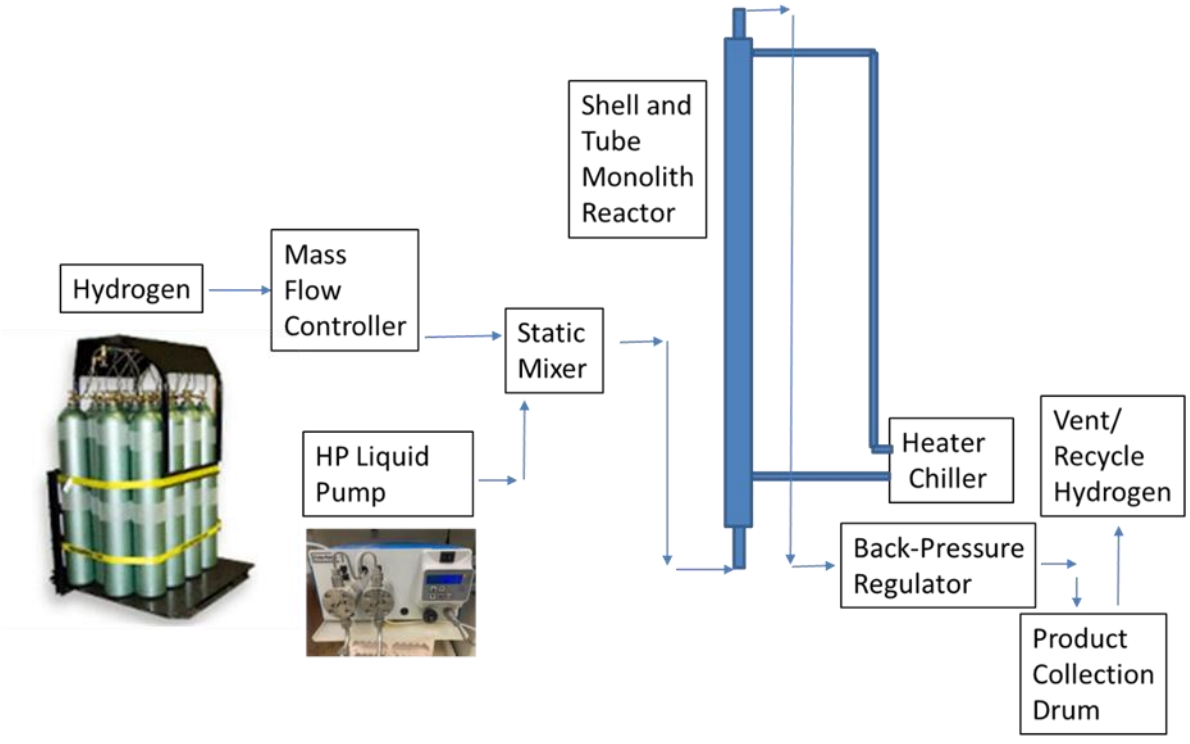
Introduction

The proprietary Oleochemical derivative is a bio-mass based resin product which can be used in the formulation of paints, coatings, composites, adhesive and lubricants. The molecular weight per unsaturated bond is 200 g/mole. The material is a liquid at room temperature, and when hydrogenated, is a solid.

Reactor System and Process Conditions

The shell and tube hydrogenation reactor system components are shown in Figure 1. The gas manifold was originally designed by Applied Catalysts and built by Parr Instruments as described in McIntosh 2010 [1] and Gulotty 2018 [2] for lab scale hydrogenation reaction testing. The apparatus was adapted to feed a shell and tube reactor pilot tube.

Figure 1. Component diagram of the hydrogenation reactor system



A 16 pack of UHP hydrogen was connected to a Brooks Mass flow controller (model 5850E) to provide hydrogen and a Cole-Parmer Model 74931-25 HPLC pump was used to flow the neat reactant liquid. The hydrogen gas and reactant liquid are passed through a static mixer and sent to the bottom of the reactor. The reactor is an 11' shell and tube reactor, containing a schedule 40 stainless steel inner tube with internal diameter of 1.18.". The stainless steel shell has an outer diameter of 2.25". A Julabo Model A40 heater/chiller containing C10 silicone heat transfer fluid is circulated in up-flow mode to heat the reactor and maintain isothermal conditions in the reactor.

The reaction liquid is also run in up-flow mode. The liquid feed and hydrogen are mixed in a static mixer and then enters the reactor at the bottom. The liquid and hydrogen then pass by an internal thermocouple surrounded by a 6" depth of stainless steel balls (1/8" diameter) to improve heat transfer in the empty tube around the thermocouple. The stainless steel balls are covered with a 20-mesh stainless steel screen that separate the balls from the catalyst, supporting the stack of monoliths in the reactor.

The catalyst used is an activated carbon monolith catalyst containing Palladium (Pd), ACMC-Pd-100-101C (230 cpsi). [3] The 10 ft bed length of catalyst was comprised of D 29 mm x L 90 mm cylindrical monoliths packed in the reactor tube with random radial cell orientation. A picture of the monoliths used is shown in Figure 2.

Figure 2. ACMC-Pd-100-101C.

Above the catalyst in the reactor is a thermocouple used to measure the outlet temperature, of the product liquid. A screen separated the thermocouple and the catalyst, the thermocouple was surrounded by stainless steel wool for heat transfer. The hydrogenated product and hydrogen not consumed in the reaction exits the reactor. At the reactor outlet is either a Swag-lok 150-300 psi check valve or Equilibar Model LF2 back pressure regulator used to control the reactor pressure at 300 +/- 50 psi. After the check valve, the product was separated from the hydrogen effluent using a 5 gallon knock-out pot. The excess hydrogen is vented, remediated, or recycled.

Over the course of the campaign, which included development runs, the liquid flow rate was varied from 2 mL/ minute to 10 mL/minute, hydrogen flow rate was varied from 1200-2200 sccm, the shell temperature varied from 175 C-215 C, the heating fluid was controlled at 200-230 °C, and the back pressure regulator of 200-350 psi. The conditions chosen for production runs was a liquid flow rate of 7 mL/minute, hydrogen flow rate of 2000-2200 sccm, shell temperature of 210-215 °C, heat fluid control temperature of 220 °C and reactor pressure of 275-350 psi. Note that the material shows evidence of decomposition if run with a fluid control temperature above 220 °C, with a brown color appearing in the product.

Portions of the solid product were analyzed for Iodine value and these values were used to estimate the degree of conversion of the unsaturated bonds. The product showed low iodine levels of 5 or less, meeting the product specification. The hydrogenated product is a white hard solid, that is brittle and can be broken into chunks by mechanical means. See picture in Figure 3.

Figure 3. Solid hydrogenated Oleochemical derivative product.

Results and Discussion

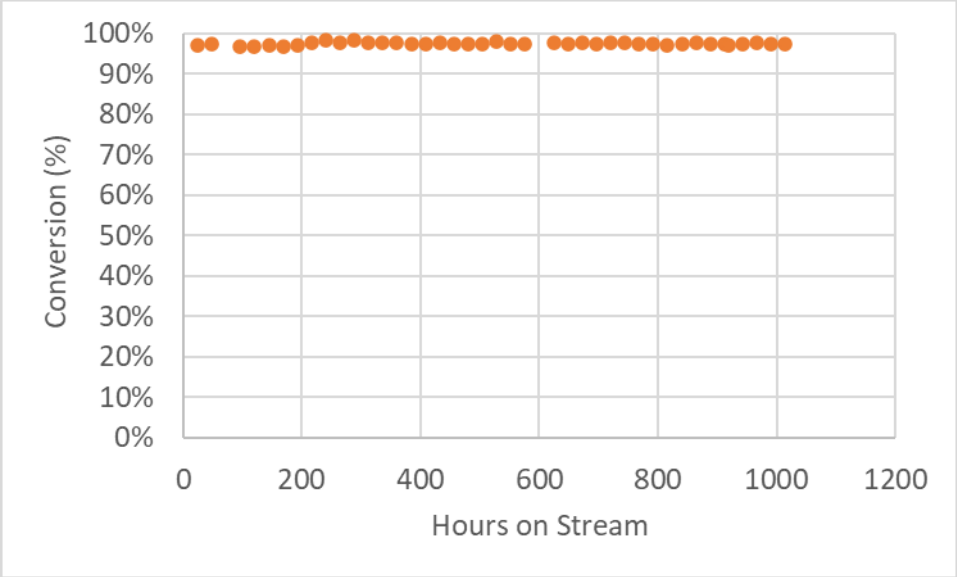
The chemistry was run over a range of shell/oil temperatures in both down-flow and up-flow mode. In the down-flow mode, the conversion was variable, from 86-97% presumably due to some of the material being pulled by gravity, shortening the residence time. In up-flow mode, a higher residence time is achieved and very reproducible conversions of 97% to 99% were achieved depending on the LHSV chosen. A plot of conversion versus liquid flow rate (LHSV hr^{-1}) is shown in Figure 4. More details are given in Table 1. The trend is well fit by a line, with conversion decreasing as the flow rate increases, and the residence time decreases. A liquid flow rate of 7 mL/ min (0.21 LHSV hr^{-1}) was chosen to yield 98 +/- 1 % selectivity for the production runs producing 2200 lb of product. Note that the pump setpoint was 15 mL/min, higher than the actual liquid flow rate of 7 mL/min, due to the high viscosity of the oleochemical derivative (~380 cP at room temperature). The hydrogen flow rate used was 2-2.2 L/min.

Figure 4. Plot of conversion versus liquid flow rate

Liquid Flow Rate (mL/min) Pump set-point	Liquid Flow Rate (mL/min) measured	LHSV hr^{-1}	Conversion (%)	Iodine Level
20	9.2	0.28	97.1	1.46 ± 0.15
15	6.9	0.21	97.8	2.91±0.08
15	6.9	0.19	97.9	2.69 ± 0.16
10	4.6	0.14	98.8	1.61 ± 0.08
5	2.3	0.071	99.5	0.67 ± 0.10
5	2.3	0.071	99.7	0.41 ± 0.06

An initial measure of the catalyst stability, by comparing the conversion measured with run time with 7 mL/min substrate flow, is shown in Figure 5.

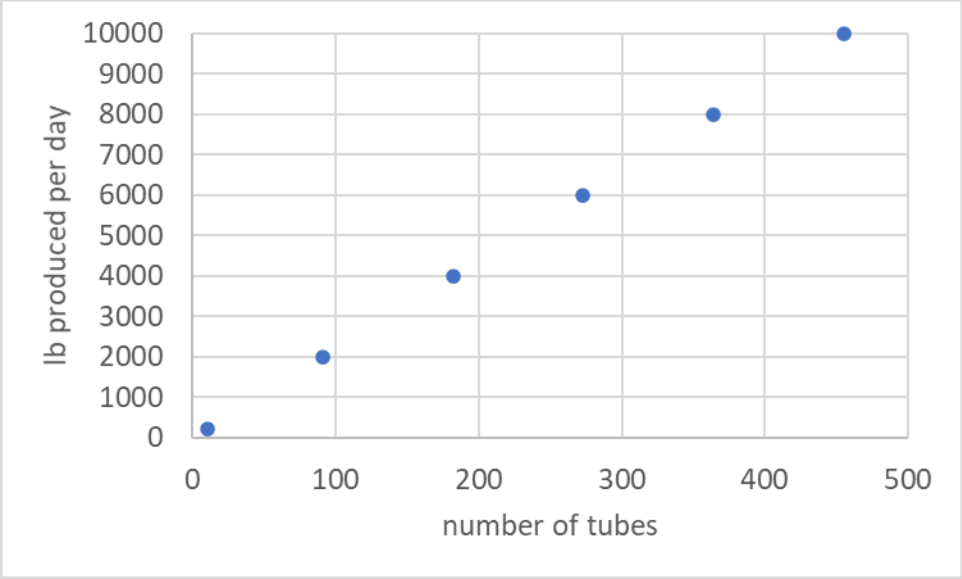
Figure 5. Conversion with time on stream at 7 mL/min flow.



Estimates of Number of Tubes for a Given Production Rate

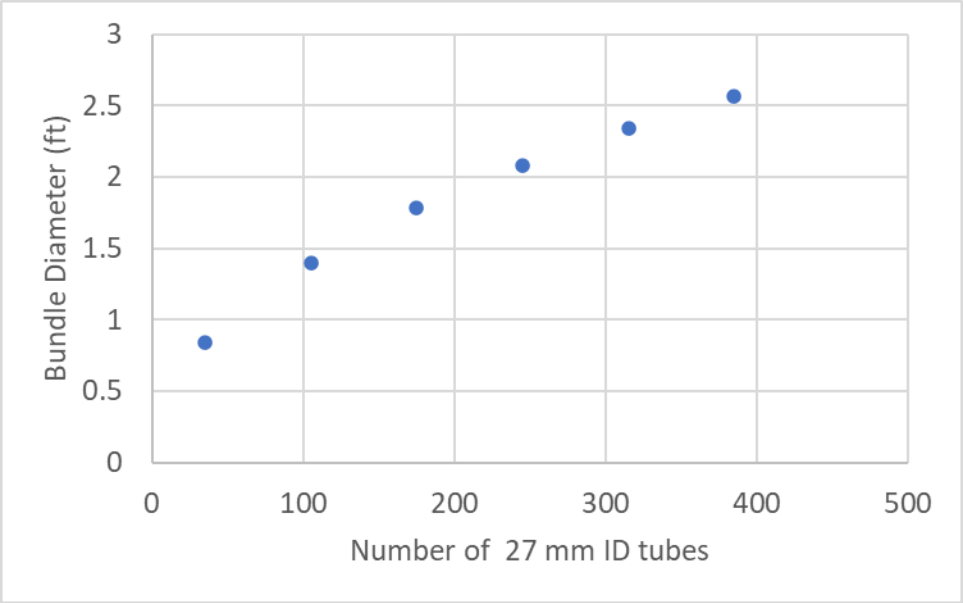
Using the results of this campaign, the number of tubes needed for a given amount of production in a commercial reactor comprised of similar reactor tubes (29 mm i.d., 10 ft catalyst bed length) can be estimated. The flow rate above of 7 mL/min, corresponds to a productivity of approximately 10 kg/ day. In Figure 6, the number of tubes needed for a given daily productivity is calculated. For example, to produce 1 ton of product per day would require a reactor of 91 tubes. Increasing the reactor tube length or diameter would allow higher liquid flow rates and increase the productivity.

Figure 6. Calculation of the Number of tubes required in shell and tube reactor to produce a given amount of product per day.



There are practical limitations to shell diameter, so it is useful to consider the shell diameter required for a given number of reactor tubes. Using front-end engineering data for this process created by R. C. Costello and Associates Inc., the shell diameter versus tube number can be calculated, see Figure 7.

Figure 7. Calculation of Shell diameter with tube number.



Summary and Comments

It has been demonstrated that 97-99% conversion can be achieved in a single pass through a 10' reactor bed containing the ACMC-Pd-100-101C catalyst in up-flow mode. The production run conditions used to make 2200 lb of product with 98+/-1.0 % selectivity to the hydrogenated product was achieved using run conditions of 220 °C shell temperature, 300 psi and an LHSV of 0.2 hr^{-1}. The catalyst showed no evidence of deactivation over a run time of 1000 hours.
From this work, an initial commercial reactor size can be estimated. For example, to produce 4 ton of product per day (~ 3 million lbs/year), a reactor comprised of 364 tubes (10 ft catalyst bed and 1.18" I.D.) would be required. This reactor would have a shell diameter of 2.5 ft.

References

1. Calculations done in collaboration with R. C. Costello and Assoc. Inc.
2. Mcintosh, S. L.; Herkes, F. E.; and Keller, J. H. "Activated carbon monolith catalysts (ACMC): A New and Novel Catalyst System." *Top. Catal.* **2010**, 53, 1091-1095.
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