T. VILELA, Avantium Catalysis, Amsterdam, The Netherlands

Quickly screen catalysts for hydrotreating of vegetable oil using high-throughput micro-pilot plants

Accurate catalyst evaluation is an important step in optimizing catalytic processes with respect to product yield, energy efficiency and overall product quality. High-throughput catalyst testing and small-scale reactors offer several advantages when compared to larger reactor systems.

Using reactors of smaller scale to evaluate catalysts with renewable feedstocks presents a clear advantage: smaller volumes reduce the amount of feed required, avoiding the typical issues associated with obtaining large quantities like handling, shipping and storage (also for longer term availability of reference feed material). Overall, small-scale parallel reactor systems like the unit described here are more cost effective than large-scale reactors.

The author's company continuously evaluates the feasibility of processing new feedstocks in its proprietary systems[a]. In this article, the results of processing blends of soybean oil and straight-run gasoil (SRGO) and 100% vegetable oil (VO) for renewable diesel production are presented.

In this testing program, a commercial ultra-low sulfur diesel (ULSD) NiMo catalyst was used to hydrotreat the VO.

METHODOLOGY

The micro-pilot plant. This testing program was conducted in a 16-parallel fixed bed reactors system with a diameter of 2 mm–2.6 mm. FIG. 1 shows a schematic overview of the 16-parallel reactors micro-pilot plant. This unit employs a proprietary high-throughput catalyst testing system[a] that enables the tight control of process conditions: temperature, flowrates and pressure.

The testing program was performed in collaboration with a global market-leading catalyst supplier. For this program, only eight reactors were used—the high-throughput 16-reactors system allows for the selective isolation of unused reactors.

Reactor loading. The catalyst packing in the single-pellet-string reactors (SPSR) is straightforward and does not require special procedures. A single string of catalyst particles is loaded in the reactors with an internal diameter (ID) that closely

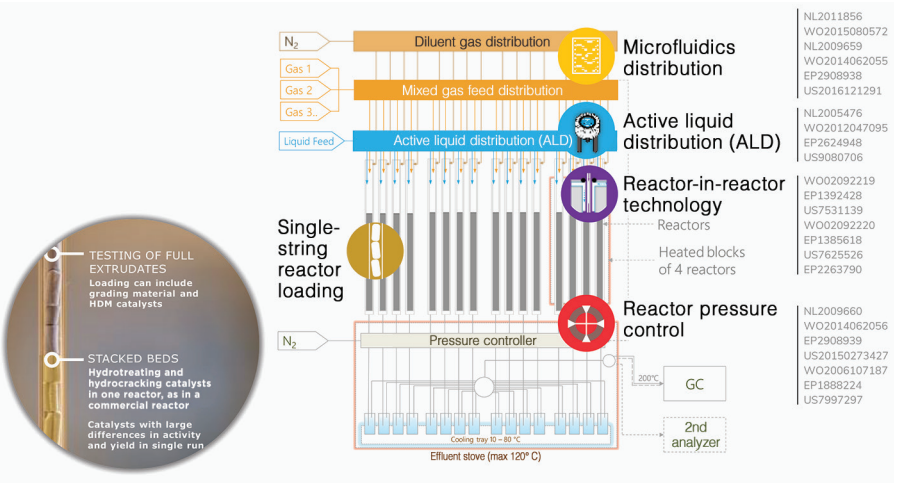

FIG. 1. Schematic of proprietary 16-parallel reactors for configured hydoprocessing applications. More information can be found in the several patents.

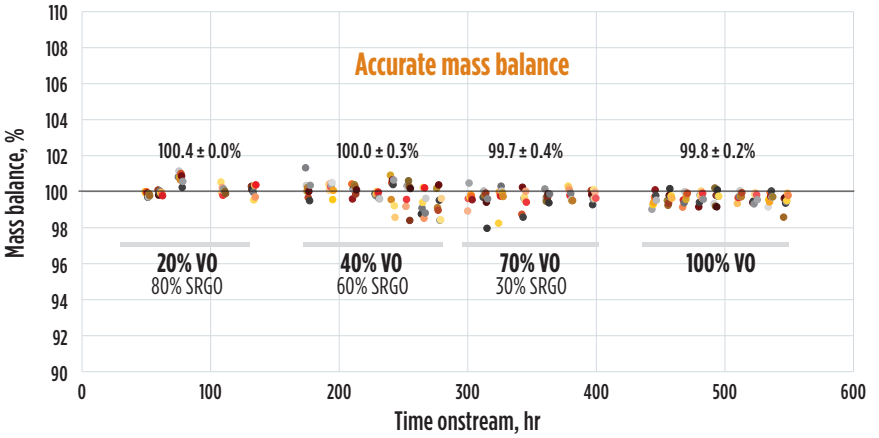

FIG. 2. Mass balance for all feedstocks tested (colors varied by reactor).

matches the particle average diameter. To enhance hydrodynamics, an inert nonporous diluent material (with a defined average particle size distribution) is used as a filler. Before conducting the final loading in a steel reactor tube, a trial loading is often performed in quartz reactors to confirm the packing (FIG. 1). The extrudates are not sorted for length or otherwise.

Operating conditions. A commercial ULSD NiMo catalyst was loaded in eight reactors (561-mm length and 2-mm ID) with two different bed lengths to test two different liquid hourly space velocities (LHSVs) simultaneously. All reactors were tested at 70 barg pressure.

Feedstock. Pressure drop is one of the main challenges when processing vegetable oils in hydroprocessing units. This is even more evident when using pilot plants with small-diameter reactors, as catalyst fouling can quickly lead to plugging. For this reason, the approach of this test was the co-feeding of the vegetable oil (soybean oil, see properties in TABLE 1) blended with an SRGO at different ratios, as shown in TABLE 2.

TABLE 2 lists the different feed blends tested over a period of 400 hr onstream (HOS) and 100% VO over 150 hr (6 d). The feed blends with 70% VO and 100% VO were spiked with dimethyl disulfide (DMDS) up to 2 wt% sulfur.

No plugging was observed in any of the small-scale reactors during the 23-days test. The high-throughput 16-parallel reactors system offers a reliable testing platform to quickly screen new catalysts for the production of renewable fuels.

RESULTS

Mass balance. Mass balance calculations ensure that the metered flows used in the calculations are accurate. An accurate mass balance is an internal control of the data quality obtained.

When calculating mass balance, various accurate measurements from both online and offline analytical equipment are composed together to accurately measure mass balance. Inherently, system errors from feed distribution to analytics require some consideration in interpreting the reported data. The main difference is that, compared to a single reactor, the distribution of liquid (i.e., the LHSV) across all the reactors has a relatively large impact on the recorded mass balance. FIG. 2 shows the overall mass balance for all reactors and the different feed blends.

The mass balance calculation includes the water in the gas stream measured with the online gas chromatograph (GC). Using the GC to measure the water content in the effluent gas is a reliable method for closing the mass balance. The gas-liquid separator was operated at optimized con-

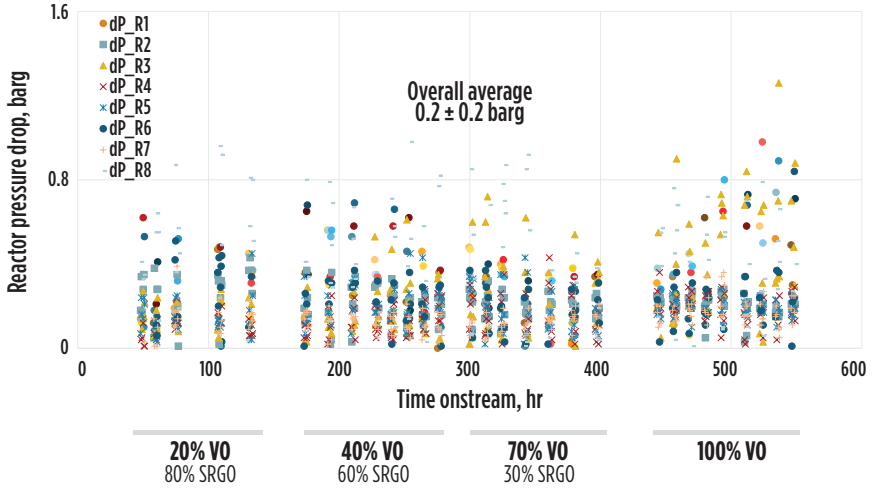

FIG. 3. Pressure drop for all eight reactors for all feedstocks tested (colors varied by reactor).

TABLE 1. Product sulfur at ULSD conditions for two VO blends

Condition	LHSV = 1 l/l/hr	LHSV = 1.5 l/l/hr
40% VO	3.3 ± 0.7 ppmw S	35.2 ± 3.0 ppmw S
70% VO	4.6 ± 0.7 ppmw S	86.4 ± 2.8 ppmw S
100% VO	1.5 ± 0.2 ppmw S	2.6 ± 0.5 ppmw S

TABLE 2. Feedstocks tested

HOS	Feed	Description
0–60	SRGO	Line out
61–110	20%VO + SRGO	20% VO testing
111–278	40%VO + SRGO	40% VO testing
279–400	70%VO + SRGO	70% VO testing
400–550	100%VO	100% VO testing

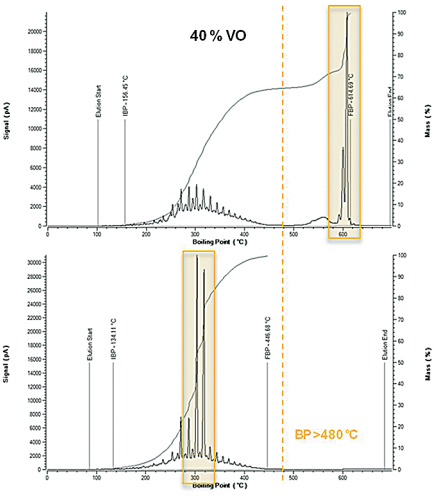

FIG. 4. Example SimDis for 40% VO feedstock (above) and the liquid product (below).

ditions during the test to evaluate the effect in the overall mass balance.

Reactor pressure regulation and pressure drop over the reactors. Reactor pressure regulation is not only important to ensure accurate pressure control at operating pressures, but also to help maintain equal distribution of the inlet flow over all reactors.

The catalyst testing system[a] includes a microfluidic-based reactor pressure controller (RPC). This patented pressure-regulation technology enables the individual regulation of the backpressure of each separate reactor at the targeted setpoint, allowing the most accurate and stable pressure control in a multi-parallel reactors system, with an average reactor to reactor pressure deviation < 0.1 barg.

Since the RPC measures the inlet pressure of each reactor, it can maintain a constant inlet pressure by regulating the backpressure. As a result, the distribution of the inlet flows over the reactors is unaffected and a low reactor-to-reactor flow variability is achieved. This also allows the measurement of pressure drop over the reactors. **FIG. 3** shows the pressure drop obtained for all reactors during the test; it can be seen that the pressure drop for all reactors is very small with an overall average of 0.2 barg.

VO conversion. At the predefined testing conditions, a total conversion of the VO was obtained without obvious effect on the LHSV. No deactivation of the catalyst was apparent with the complete test duration. **FIG. 4** shows an example simulated distillation (SimDis) for the 40% VO feedstock where the conversion of triglycerides (BP > 480°C) into paraffins (apparently mostly C_{16} to C_{18}) can be seen.

Liquid product yields. FIG. 5 presents the diesel, kerosene and naphtha yields for 40% VO, 70% VO and 100%VO feedstocks. Key findings include:

- The yield to diesel is ~80% for the 100% VO feedstock
- Liquid product analysis (ASTM D5291) confirmed that there was no oxygen left
- As expected, no naphtha or kerosene was produced from the conversion of the VO; there is a direct conversion of triglycerides to C_{12}+ paraffins
- Small effect of the higher LHSV (1.5 l/l/hr) on the VO products yield
- Overall a good reactor-to-reactor repeatability for the product yields.

Gas product yield. FIG. 6 shows the gas make yield (C_1, C_3 and C_4) for all feedstocks tested [only traces of C_2 were observed (not presented in the graph)]:

- As expected, methane (CH_4) and propane (C_3H_8) are the main gas hydrocarbons products
- Increasing gas product yields as the amount of VO is increased on the feed
- Up to 5 wt% C_3H_8 produced when processing 100% VO

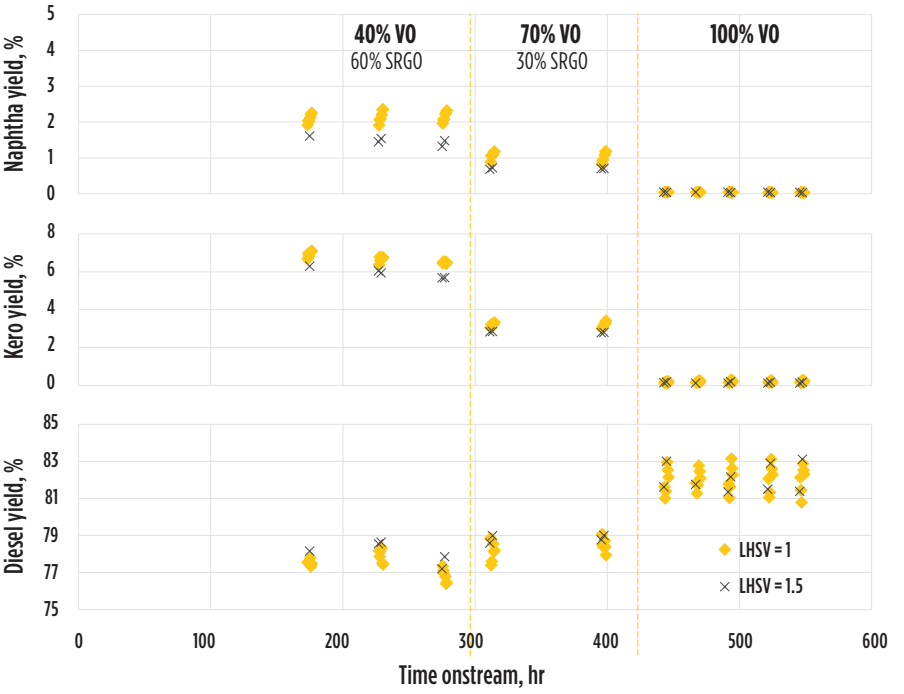

FIG. 5. Liquid product yields.

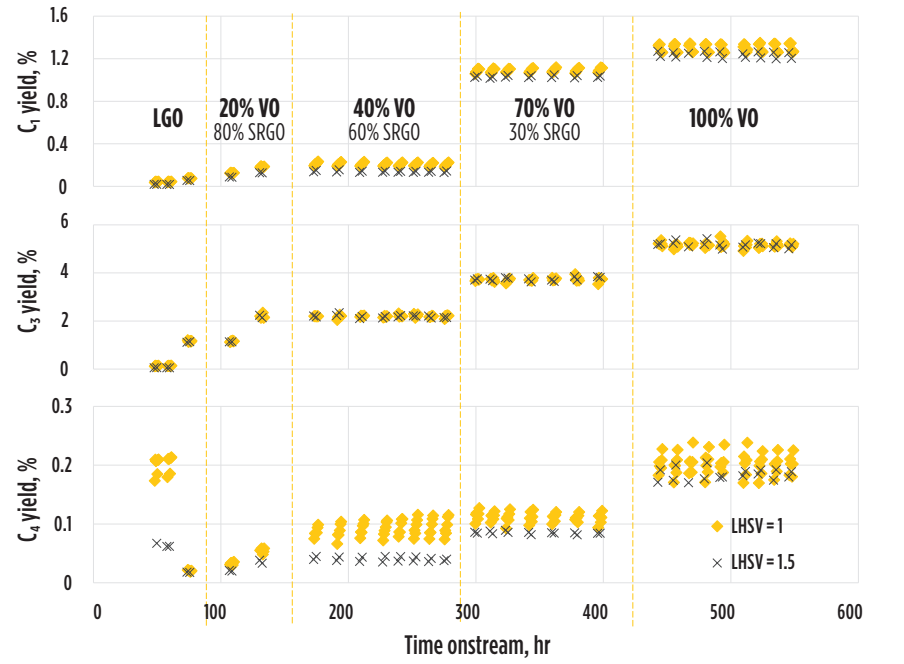

FIG. 6. C_1, C_3 and C_4 gas product yields.

- Good reactor-to-reactor repeatability for the gas product yields
- Small but consistent effect of LHSV on the gas yields.

FIG. 7 shows the carbon monoxide (CO), carbon dioxide (CO_2) and water (H_2O) yields:

- Increasing gas product yields as the amount of VO increases
- Up to 3 wt% CO and 5 wt% CO_2 produced when processing 100% VO
- The yield to water presented does not include the small amount of water remaining in the liquid product
- Good reactor-to-reactor repeatability for the gas product yields
- Clear differences in CO and CO_2 yield when using a higher LHSV.

Hydrogen (H_2) consumption. H_2 consumption was measured using the online GC by comparing the outlet flow of $H_2$with the inlet flow. **FIG. 8** shows that a step increase in the H_2 consumption can be expected with an increasing amount of VO in the feedstock:

- Approximately 20% of the H_2 fed into the system is consumed when processing the 100% VO feed
- Good reproducibility for H_2consumption among duplicated reactors
- Clear effect of LHSV on the light gasoil (LGO) and LGO blends hydrotreating.

Product sulfur. The product sulfur was measured for the 40%, 70% and 70% VO blends at ULSD conditions. Note the very good repeatability of the sulfur results for the duplicate reactors at such high conversion:

- The reactors' temperature was adjusted to produce < 5 ppmw sulfur for the LHSV = 1 l/l/hr
- Very good reproducibility for product sulfur among duplicated reactors.

Takeaways. No plugging was observed in any of small-scale reactors during the 23-d test with various VO blends and 6 d of running 100% VO. Quantifying the amount of water in the gas effluent using an online GC is a feasible method for closing the mass balance. The accuracy of the mass balance and yields obtained during the test are similar to conventional hydroprocessing catalyst testing. High-temperature SimDis is a feasible method for evaluating the conversion of triglycerides during VO hydrogenation tests. The test allowed accurate measurement of the hydrodesulfurization (HDS) capacity of the catalyst at start-of-run (SOR) conditions when processing LGO / VO blends.

The proprietary high-throughput 16-parallel reactors system[a] produces consistent and reliable high data quality with excellent reactor-to-reactor repeatability for the hydrotreating of VO, and offers a reliable testing platform to quickly screen new catalysts for the production of renewable fuels. HP

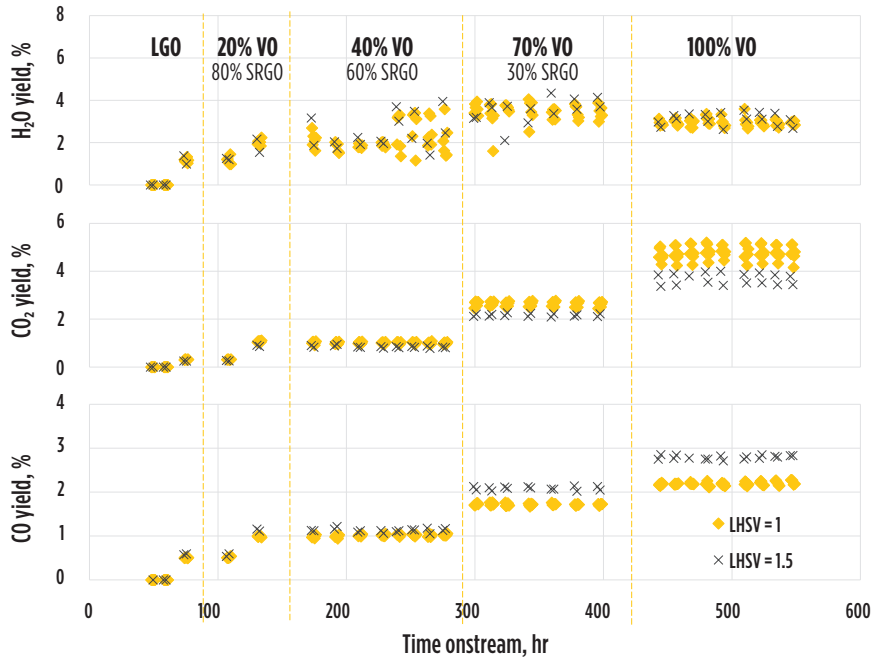

FIG. 7. H_2O, CO_2 and CO gas product yields.

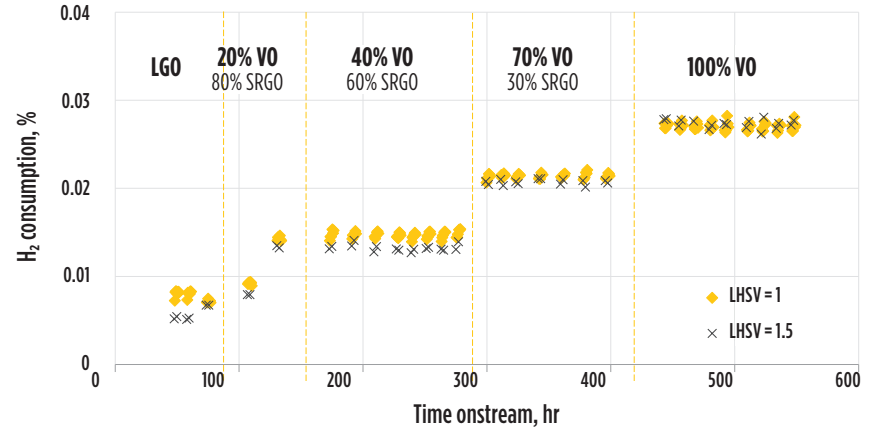

FIG. 8. Online H_2 consumption.

NOTES

[a] Avantium Catalysis' Flowrence® systems.

TIAGO VILELA leads the Refinery Catalyst Testing (RCT) global services for Avantium Catalysis and is accountable for the overall performance of the business line. Dr. Vilela has more than 19 yr of experience in engineering, project management, management consultancy and business development. Before joining Avantium, he worked as a Senior Asset Management Consultant for Jacobs and as a Management Consultant for AP-Networks. He has advised on numerous projects and maintenance turnarounds around the globe, helping clients to improve their project, turnaround and operational readiness performance. Dr. Tiago holds an MS degree in chemical engineering from the University of Aveiro, Portugal, and a Professional Doctorate in Engineering degree from Delft University of Technology.