

Industrial-scale production of renewable diesel

A revamp has made possible the large-scale production of clean diesel with a significant percentage of renewable content

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A renewable diesel has emerged as a drop-in substitute for today's mineral diesel fuels. Its production is not limited to seed oils, but is flexible in that it can use a number of different feedstocks with very little change in operating conditions yet still produce a renewable and clean product. Renewable diesel is produced by hydrotreating, whereby the oxygenates in bio-feedstocks are hydrogenated into hydrocarbons. Hydrotreating takes place in existing diesel hydrotreaters in a co-processing scheme, where the biofeed component is deoxygenated and the fossil diesel component is simultaneously desulphurised, or it can take place in a standalone unit processing 100% biofeed. In both cases, conversion occurs over hydrotreating catalysts and in conditions similar to those used in hydrotreaters today. The product can, in some cases, require its cold flow properties to be upgraded by, for instance, catalytic dewaxing.

Haldor Topsøe has supplied catalyst for a number of operating units producing renewable diesel and has also licensed process technology for standalone units and revamps to enable co-processing. An earlier article in *PTQ* (Q2 2010, p101) discusses the chemistry, catalyst technology and challenges of renewable diesel hydrotreating. This article describes how innovative technology solutions were implemented at the Preem Gothenburg refinery. Operating data from the current cycle explain how the revamp at Gothenburg has made possible the large-scale

production of clean diesel with a significant percentage of renewable content.

Rebuilding for renewables

This case study shows how the challenges of renewable diesel hydrotreating can be overcome through technology solutions and the use of a specifically designed catalyst series. It also serves as an example of how a non-edible and low-value stream can be upgraded into a high-value transportation fuel by hydrotreating. Preem contacted Topsøe in order to scope

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out the possibilities of revamping an existing mild hydrocracking unit to a green hydrotreating unit, where large quantities of raw tall diesel (RTD) could be co-processed together with light gas oil. The capacity of the unit is approximately 10 000 b/d, and a target was set of co-processing up to 30% RTD in the feed. A development agreement was signed, stipulating that Topsøe would carry out the basic design of the unit.

RTD is produced from tall oil by Sunpine from Kraft paper mills in the north of Sweden. Tall oil mainly consists of resin acids and free fatty acids, as well as a number of contaminants in smaller concentrations. Through an esterification process, the majority of the free fatty acids are converted to fatty acid methyl esters (FAME), while the resin acids are left almost unconverted. RTD differs from other feedstocks used for renewable diesel production in that it is non-edible, and thus this technology does not affect the global food shortage negatively or add to food prices. The composition of RTD varies, depending on the type of wood used in the paper mill and the severity of the esterification process. Unlike other bio-oils, RTD also contains several hundred ppm sulphur. Thus, flexibility was needed to ensure that all feed types could be processed. This was verified in the pilot plant phase, where several different compositions of RTD were successfully converted, confirming the performance of the catalyst and the revamp design.

The design has enabled Preem to co-process 30% RTD with light gas oil to produce a renewable diesel meeting all ULSD EN 590 diesel specifications. A level of 30% is a relatively high fraction of biofeed in an existing unit not built to handle this type of feed, and unique challenges were encountered, in particular related to hydrogen consumption, exotherm, catalyst selection and corrosion, both upstream and downstream of the reactor. The revamped unit was started up in 2010.

Handling of corrosive feed and high exotherm

The introduction of RTD poses a special challenge with regard to procedures for material selection, as this is a very unconventional feed with a very high total acid number (TAN). It contains many unconverted free fatty acids, as well as resin acids, which may increase the corrosion rate in pipes, heat exchangers and the fired heater upstream of the hydrotreating reactor, where these compounds are converted. The corrosion issue has, in other cases, been design-limiting when deciding the amount of tall

control the TAN and thereby minimise corrosion. Since RTD is only injected after the fired heater and as a liquid quench to the second reactor bed, the hardware has very limited exposure to the highly corrosive RTD. Thus, only minor changes to the material selection were necessary. These changes meant that the unit is prepared for, and has already experienced, operation with an even higher fraction of RTD feed.

Following its revamp to renewable diesel production, the unit operates at a lower average temperature, but with significantly higher

quench, which makes it possible to control heat release from the exothermic reactions, thereby lengthening the lifetime of the hydrotreating catalysts by a significant degree. With fresh RTD used as a liquid quench between the first two beds, more hydrogen can be used upstream of the reactor to increase the hydrogen partial pressure. This measure helps prevent gum/coke formation and corrosion, thereby ultimately delivering higher unit reliability and lower investment cost.

Selection of catalysts

The implementation of new process technology solutions goes hand in hand with the selection of catalysts, as catalyst activity and selectivity determine the necessary reaction conditions and the composition of reactor effluent. The conversion of high levels of RTD in the feed constitutes a very fast reaction, consuming substantially higher amounts of hydrogen than in the case of conventional hydrotreating, and this requires specialised catalysts for the conversion of renewable material. The correct balance between activity and stability depends on the feed and conditions and has important implications for the operation of the unit.

For the Gothenburg unit, Preem chose a catalyst loading consisting of an extended grading system, Topsøe's TK-339 and TK-341 renewable fuels catalysts and a Topsøe high-activity Brim NiMo catalyst. The NiMo catalyst ensures that sufficient HDS activity is available to reach a 10 ppm sulphur target throughout the cycle. Since the RTD is split between the first two beds, the reactions in both of the top beds are quite similar, and the catalyst loading is also almost the same. The renewable fuels catalysts are optimised for high stability and do not possess an equally high HDS activity as the latest generation of Brim-type catalysts. However, if a simple old-generation catalyst with a low activity is used, the conversion of RTD is merely shifted to the bottom of the reactor, where the high-activity catalysts are situated. Thus,

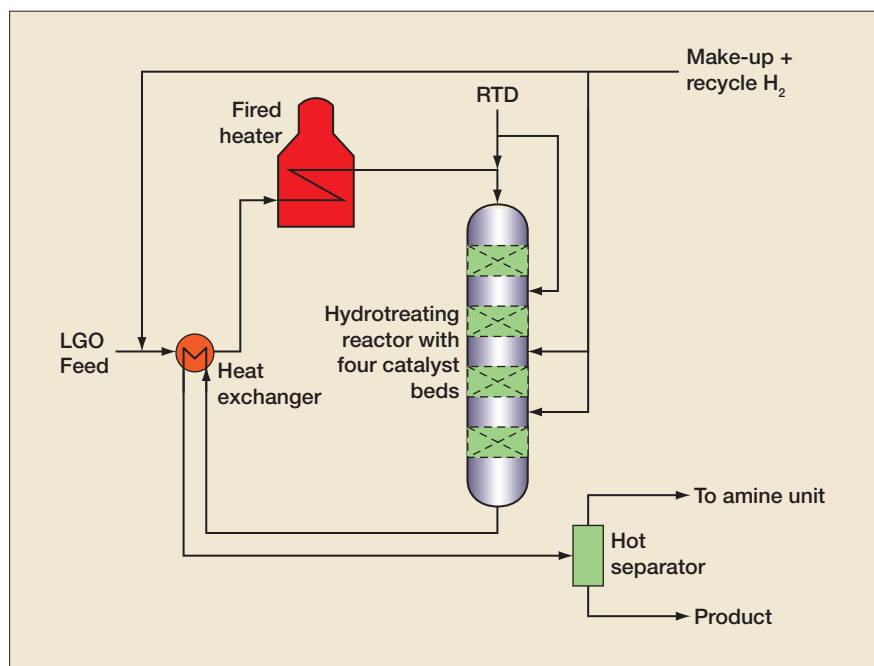


Figure 1 Revamped hydrotreater for RTD co-processing at Preem Gothenburg refinery

oil or derived material that can be co-processed. Therefore, a high priority was to design the feed system to overcome these challenges.

A special RTD feed system was designed for this purpose by Preem and Topsøe. Injection of RTD and mixing with the mineral feed is carried out in multiple steps (see Figure 1). Part of the RTD is introduced at an injection point after the fired heater and prior to entering the reactor. In this way, all existing process equipment upstream of this injection point is left unaffected. The remaining part of the RTD feed is introduced between the first two beds of the reactor to control the temperature profile, but also to

hydrogen consumption. As a result of exothermic hydrodeoxygenation reactions, the heater duty and fuel consumption of the unit are lower compared with what is seen in normal hydrodesulphurisation mode. This means that the added reaction heat is also utilised in fossil light gas oil hydrodesulphurisation, so this operation is less energy consuming. However, the large amount of heat released due to the hydrogenation of RTD in the reactor must be controlled by a proper quench system. Although the main purpose of splitting the RTD into several streams and delaying the mixing is to eliminate the risk of corrosion, another equally important purpose is to provide a liquid

coking and delta P build-up in this part of the reactor must be foreseen. Tests in a semi-adiabatic pilot unit demonstrated that the chosen catalyst system was able to gradually convert the RTD, indicated by a linear temperature increase down through the reactor bed. The tests also showed that this configuration was very stable and was operable for extended periods without pressure drop issues.

Implications of increased CH₄, CO and CO₂ formation

The reactions of RTD result in the formation of water and oxygen-containing gases such as CO and CO₂. Both CO and CO₂ pose problems that had to be solved through process modifications. The unit is equipped with an amine wash for the removal of H₂S, and this operation will also remove a large fraction of the CO₂ formed in decarboxylation reactions. However, downstream of the reactor CO₂ can form carbonic acid if liquid water is present. This means that the risk of carbonic corrosion in the air cooler and cold separator is high and proper measures had to be taken to eliminate this risk.

The increased amount of methane produced will build up in the recycle gas loop if a sizeable purge is not used. CO can be removed by a chemical transformation but, in this case, the increased purge rate was sufficient to keep the CO at a tolerable level. Furthermore, the choice of catalysts ensured that CO inhibition and the associated activity penalty did not become an issue. However, in downstream units, CO can cause problems, and the implications of this must be scrutinised. The existing purge gas recovery unit is a cryogenic unit that cannot remove CO and, since the purge gas is used in another refinery unit where CO would be a catalyst poison, a way of removing CO had to be implemented.

To remove CO from the purge gas stream, Topsøe designed a methanator, where CO reacts with hydrogen to form methane by the following reaction:

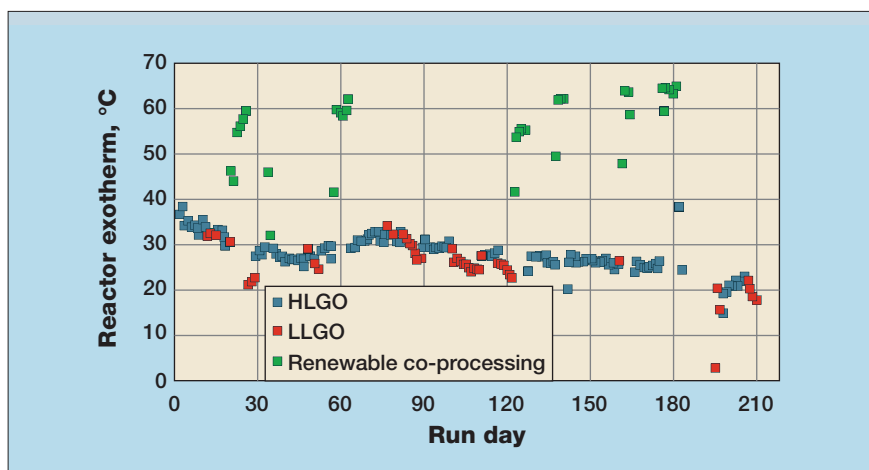
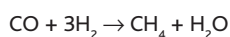


Figure 2 Reactor exotherm versus run days

This elimination of CO by means of a nickel-based methanation catalyst relies on experience in the design of ammonia plants, where methanation can be regarded as a proven technology. Alternatively, these components can be removed by pressure swing absorption (PSA) if the refiner has spare capacity in a PSA unit.

Operating experience with renewable diesel at Gothenburg

General operating strategy

The reactor was successfully loaded, the catalysts were sulphided and the unit was brought on-stream in May 2010. The unit operates in several modes in order to process

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different streams into various products. Generally, three modes of operation are employed: a light cut of a light gas oil (LLGO), a heavy cut of a light gas oil (HLGO) and renewable diesel. In the latter mode, LLGO is co-processed with the biofeed. As an additional challenge, the RTD feed was not available for processing at the start of the cycle,

so it was decided that rapeseed oil-derived fatty acid methyl esters (RME) should be processed instead. A design check of the revamped unit showed that there were no major issues in using RME as feedstock, although a somewhat higher CH₄ yield can be expected compared with the RTD case. This demonstrates the feed flexibility of the hydrotreating approach to making renewable fuels, which reduces the commercial risk of the operation, since it does not depend on a single source of feedstock.

Apart from a few weeks of planned shutdown, the unit has been on-stream since the start-up and been continuously operated in all three modes. The unit's performance has been very satisfactory and in good agreement with design predictions. In the following sections, key performance data are shown to illustrate how the challenges usually faced in renewable co-processing have been overcome.

Reactor exotherm and hydrogen consumption

Figure 2 shows the reactor exotherm for the different operating modes. As can be seen, the exotherm is much higher in renewable mode due to the hydrodeoxygenation reactions. Most of this exotherm is related to reactions in the first two beds. In HLGO and LLGO modes, the operation of the unit is quite stable and the slightly lower exotherm towards the end of the period is related to slightly different operating conditions and type of crude processed. The measured

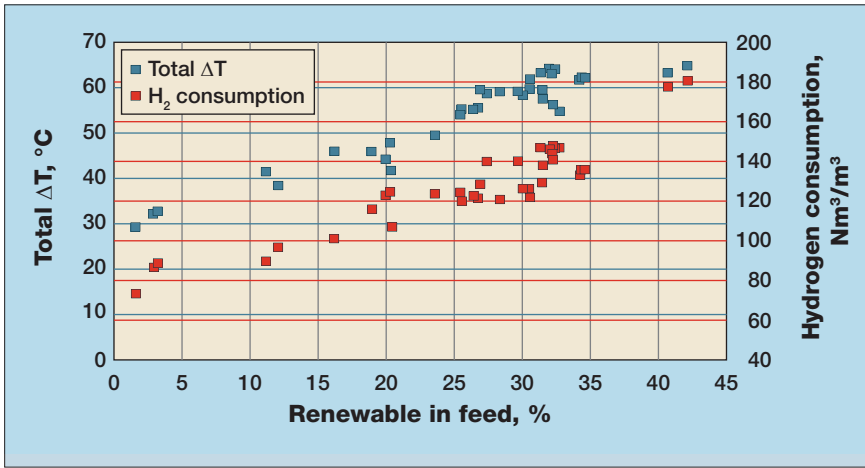


Figure 3 Reactor exotherm and hydrogen consumption vs vol% of renewable component in the feed

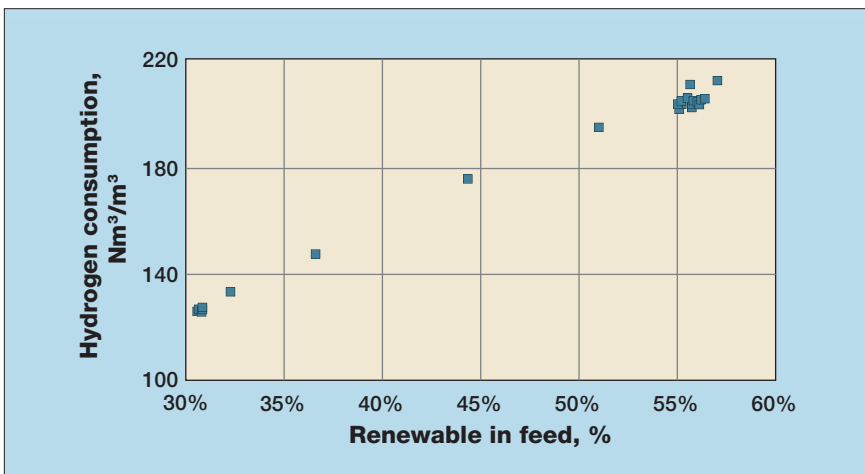


Figure 4 Hydrogen consumption during trial with high amounts of RTD

exotherm is in good agreement with the design value.

It was more attractive to Preem to produce a diesel product with a high renewable content for shorter periods than to run with a lower content for longer periods. Figure 2 demonstrates that this strategy has been implemented and that it is

possible to shift quite frequently between different modes of operation, despite the significant difference between feeds.

Since all of the hydrogen-consuming reactions are exothermic, the exotherm is closely related to hydrogen consumption. In the production of renewable diesel,

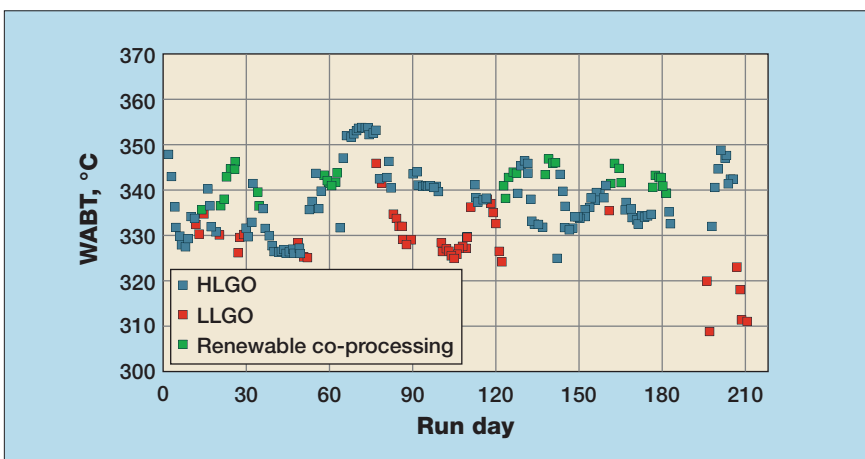


Figure 5 Weighted average bed temperature

both exotherm and hydrogen consumption are directly related to the amount of renewable material in the feed. Figure 3 shows how the unit has been co-processing a widely varying amount of RTD and RME, and how the exotherm and hydrogen consumption have responded to this. Clearly, a quite excessive strain is put on the heat management and hydrogen requirements when co-processing even minor amounts of RTD or RME. At the targeted 30 vol% co-processing level, hydrogen consumption was in line with pilot plant testing and design predictions.

Although the target was originally to co-process no more than 30% of RTD, a small test was made to evaluate the possible use of higher amounts of RTD. Figure 4 shows that up to 55% of RTD has been processed, with an associated increase in hydrogen consumption. Based on this trial, it was concluded that the unit responded well and can be expected to be able to handle these higher amounts for longer periods of time, but, of course, this will require a higher availability of hydrogen.

Catalyst activity and deactivation

Since catalyst HDS activity must be sufficient to reach 10 ppm sulphur in all modes throughout the cycle, it is important to monitor constantly feed, conditions and product properties. Topsøe aids in evaluating this data and in following the development in catalyst activity. Based on this, recommendations are made to ensure that, for instance, maximum catalyst life or maximum number of barrels processed is reached. In this case, where different feed modes are used and where renewable co-processing increases the risk of catalyst deactivation when generic catalyst types are used, it is particularly important to monitor the catalyst activity closely.

Figure 5 shows how the weighted average bed temperature (WABT) has evolved in the cycle so far, and shows that fairly equal temperatures have been used in the three modes of operation. The HLGO mode requires slightly higher temperatures than the LLGO mode.

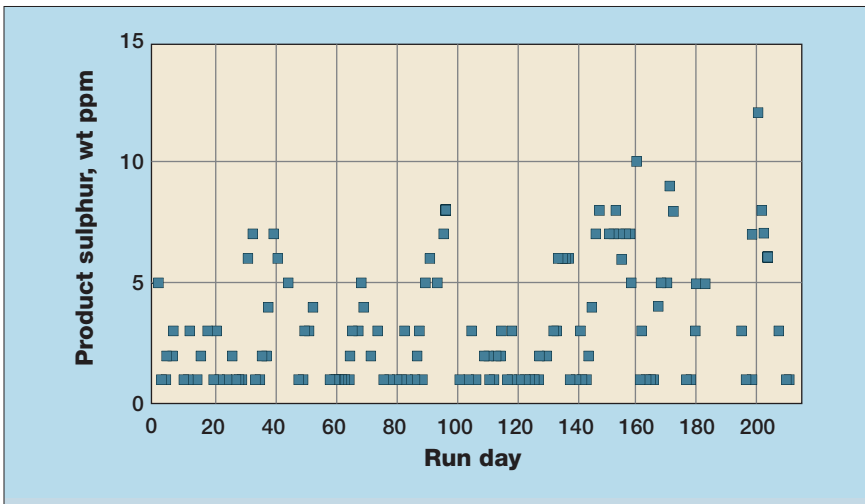


Figure 6 Product sulphur content

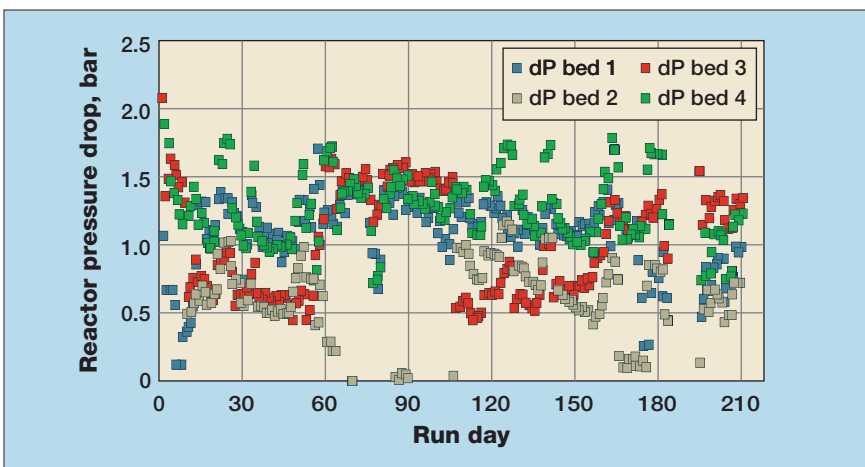


Figure 7 Pressure drop over four catalyst beds

The product sulphur content is shown in Figure 6. The target of 10 ppm sulphur is reached in all three modes and does not show any increasing trend with time, other than can be explained by changes in operating conditions. When calculating the normalised WABT, the HLGO is quite clearly 10–15°C less active than the LLGO mode.

However, the normalised WABT in the LLGO mode is quite similar to that seen in the renewable mode, which means that the catalyst is not inhibited by the renewable component or by any of its products.

When taking the variation in feed properties and process conditions into account, catalyst deactivation is as guaranteed or lower, and the

deactivation appears to proceed gradually and is not accelerated by running in renewable mode.

Pressure drop

With the introduction of fast and very exothermic reactions in the top two beds during renewable co-processing, it is particularly important to monitor the build-up of pressure drop, as any gum or coke formation can quickly lead to an increased pressure drop, which in turn will lead to very short cycle lengths. As described above, this was an important point in the technology design and catalyst selection. It was also a parameter that was monitored during pilot testing.

The data shown in Figure 7 illustrate that there is a great deal of variation in the observed pressure drop, mainly attributable to experimental scatter. Most importantly, there is no increasing trend with time and no sign that any permanent dP build-up is taking place. Also, the pressure drops over all four beds are comparable and not higher over beds 1 and 2, where the conversion of renewable material is taking place.

To further elucidate the causes of the trends in the observed dP, Figure 8 shows the total pressure drop along with the feed rate and fraction of renewable content in the feed. As can be seen, most of the variation in pressure drop is related to the changing feed rate. When operating in renewable mode, a much higher treat gas rate is used, and the pressure drop thus also increases. However, this is a purely temporary phenomenon and, when returning to LLGO or HLGO mode, the pressure drop returns to a lower value and no permanent increase is observed.

A test run was performed to validate the design and demonstrate that all design predictions could be met. This test run was performed with 32 vol% RTD and showed that all design guarantees were met, including hydrogen consumption, yields, RTD conversion and all guaranteed product properties such as sulphur content. In short, all concerned are satisfied with the performance of the revamped unit,

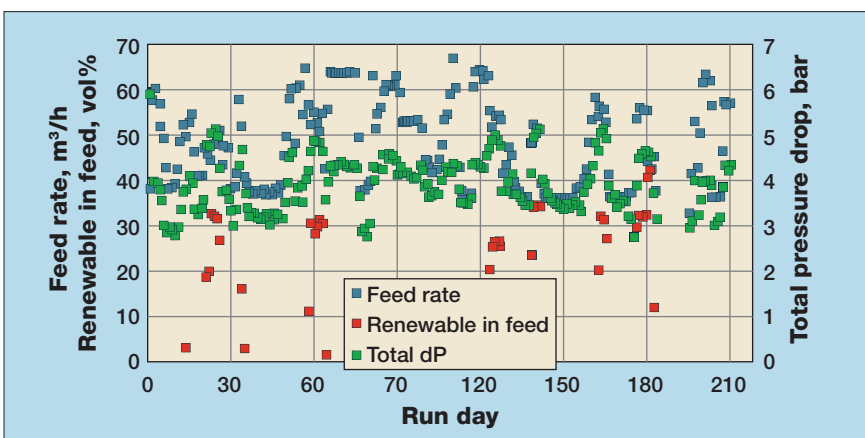


Figure 8 Total pressure drop, feed rate and amount of renewable component in feed

proving the successful implementation of a large-scale production of a middle distillate fuel with a high content of renewable diesel from a non-edible waste material. The production of a renewable diesel does not increase deactivation or dP build-up rates and is fully integrated with the desulphurisation of conventional petroleum diesel.

Conclusions

Renewable diesel from the hydrotreating of biofeedstocks is a drop-in fuel that can replace mineral diesel using existing infrastructure and conventional engine technology. A co-processing scheme reduces energy consumption and increases the energy efficiency of the unit. The process is versatile in terms of feed type and thus offers great potential for future operation on, say, algae oils or other unconventional second-generation feedstocks.

When compared with conventional hydroprocessing of petroleum diesel to make ULSD, the conversion of fast-reaction oxygenates requires

quite different catalyst characteristics and poses new challenges with respect to equipment and process design. If unaddressed, the consequences of introducing new reaction chemistry, such as high hydrogen consumption and large exotherms across the catalyst beds, will quickly lead to catalyst deactivation and fouling. An important tool to overcome these issues is the development of speciality catalysts for renewable fuel operation to ensure low deactivation rates and a high stability towards fouling. These catalysts may be combined with a high-activity Brim catalyst to ensure that ULSD is produced and also with the dewaxing catalysts TK-928 and TK-932, which, through isomerisation, will provide the necessary improvement in cold flow properties to meet cloud point specifications.

BRIM is a mark of Haldor Topsøe.

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