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SEEING THE WOOD FOR THE TREES

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Pine is a softwood, grown in abundance in the southeastern part of the US using sustainable methods pioneered by the pulp and paper industries. However, this industry is declining due to lower demand, leaving significant forest resources available to use in a new way.

Anellotech has developed a thermal-catalytic process that converts solid non-food biomass material into hydrocarbon naphtha and middle-distillates using a fluid-bed reactor. Loblolly pine is feedstock for the first-generation implementation of the Bio-TCat™ process (Figure 1), giving it the advantages of using existing supply chains and mature mechanical harvesting and processing technologies used by paper and wood pellet manufacturers. In the future, the technology could be developed for other types of wood, lower value wood byproducts, non-food agricultural residues, and energy crops.

After pre-processing the wood to reduce inorganic contaminants that would otherwise poison the catalyst, the biomass is dried and ground into particles that are injected into a fluid-bed reactor. A combination of thermal cracking, pyrolysis, and catalytic reactions converts solid biomass into hydrocarbon products which exit the reactor in the vapour phase. The reactor contains a custom zeolite catalyst formulation jointly developed by Anellotech and Johnson Matthey. The fluid-bed catalyst is rapidly deactivated by coke deposits that are a byproduct of biomass conversion. However, the coke is readily removed by oxidation in the catalyst regenerator. Catalyst continuously circulates between the reactor, a catalyst stripper for removing adsorbed hydrocarbons, and the regenerator via standpipes and controlled by slide valves, in a manner analogous to fluid catalytic cracking (FCC). The Bio-TCat reactor uses relatively long contact time compared to FCC or conventional biomass pyrolysis processes, resulting in significant deoxygenation of the biomass. This efficient single-reactor conversion step avoids formation of intermediate unstable oxygen-rich bio-oil, which enhances yield of desired products, minimises capital, and avoids expensive high pressure hydro deoxygenation.

After vapour quenching and recovery, the liquid product mixture undergoes mild hydrotreating to remove trace organic sulfur and other impurities that originated with the biomass. AnelloMate™ low sulfur naphtha is suitable for use as a gasoline blendstock, or can be used as feed to an aromatic separation plant to provide renewable benzene, toluene and xylene (BTX) base chemicals for renewable plastic manufacture. For gasoline blendstock, the naphtha is directed to a C6 splitter (Figure 2). The benzene rich overhead from this column is either sent to an aromatics separation plant for recovery of the benzene or saturated with hydrogen to produce cyclohexane-rich light naphtha for blending into the gasoline pool. The C7 – C9 splitter bottoms product can be blended directly into the gasoline pool.

The distillate product can be used directly as fuel oil or low-sulfur marine fuel, or refined further into jet fuel or on-road diesel blendstock by hydrogenation to convert alkyl-naphthalenes to more desirable hydrocarbons.

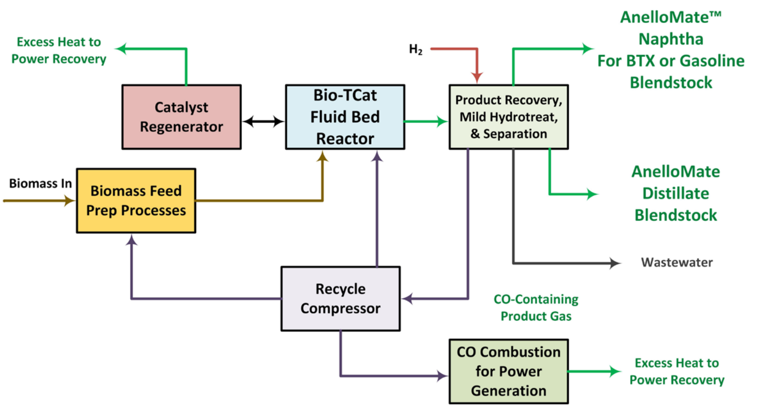

Figure 1. Block diagram of the Anellotech Bio-TCat process.

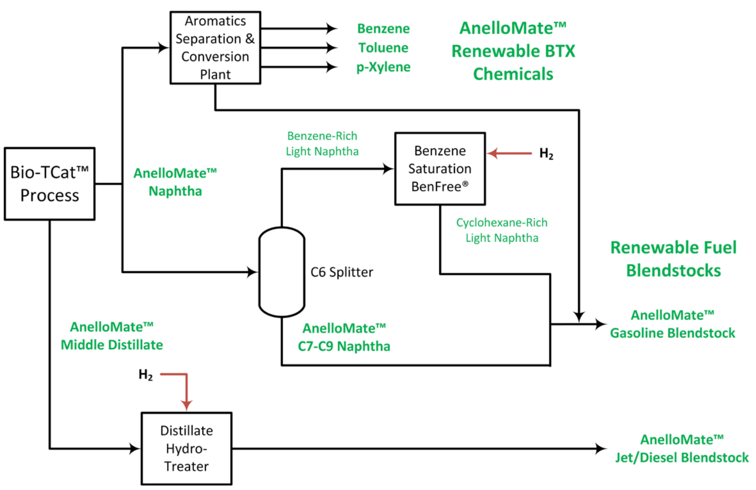

Figure 2. Bio-TCat Fuels and chemical process diagram.

Process development

A large-scale development unit, TCat-8® (Figure 3), has been operating at the South Hampton Resources (SHR) chemical plant in Silsbee Texas, US, since 2017. Anellotech and IFP Energies nouvelles (IFPEN) engineers, with assistance from SHR operators, have been running the unit to convert wood into hydrocarbons, performing mass balances, collecting data needed for commercial scale design, and filling drums with hydrocarbon for product development work. In results to date, the TCat8 plant performance has achieved target product yields and catalyst on-stream performance at commercial operating conditions. Experience and insights into other aspects of operation such as process control, plant safety, and process reliability have been obtained and are important factors for commercial operation and design.

In 2018, the unit had operated for over 2000 hr with continuous catalyst circulation and daily catalyst makeup addition and removal to manage catalyst activity at the target level. Equipment includes a fluid bed reactor, catalyst stripper, and catalyst regenerator, quench tower, recycle compressor, and online analytical instrumentation. Reactor yields are measured multiple times per day over an equilibrated catalyst and mass balance closures of 100% ±2% are routine. The unit operates 24/7 inside an OSHA PSM compliant facility.

These results were achieved with loblolly pine harvested from Georgia forests. Anellotech's MinFree™ pretreatment process, operational at multi-ton scale, has been used to ensure low mineral content in the feedstock, which is critical for catalyst performance.

The onsite involvement of IFPEN engineers in the test programme – together with parallel development efforts in other areas of process scale-up including hydrodynamic cold flow measurements, CFD modelling, and thermodynamic phase-equilibria data for process simulations – has brought significant benefits to the programme. Axens, the international process licensing, engineering and catalyst firm (an IFPEN subsidiary), is carrying out process engineering development leading to the scale-up design for commercial Bio-TCat facilities.

Johnson Matthey jointly developed with Anellotech the catalyst formulation and produced it in commercial scale facilities for use in the unit, thereby minimising the risks of catalyst production scale-up. The company has also been involved in monitoring catalyst performance with time on stream to characterise performance, identify long-term deactivation mechanisms, and identify future improvement areas by developing new formulations that are tested in the research laboratory. Thus, every major aspect of process technology development is included in the programme, including biomass pre-treatment, biomass injection into the fluidised bed reactor, reactor and regenerator scale-up, process modelling, catalyst formulation and production, pilot plant testing, catalyst makeup and activity management, process control, product recovery and upgrading, and analytical chemistry.

Greenhouse gas reductions

The Bio-TCat process has a CO_2 emission reduction potential of 90% or more for transportation fuels when compared to petroleum-derived equivalents on a well-to-wheel basis. A lifecycle assessment (LCA) of the process's greenhouse gas (GHG) emissions was first conducted for a forest-to-wheel basis using mass and energy balance information from a detailed commercial-scale process design produced using process simulation software, and emission factor data from various government and private databases. Jacobs Consultancy, a subsidiary of Jacobs, conducted an in-depth review of Anellotech's methodology, data, and calculations. Jacobs then used its own industry-accepted refinery and petrochemical models to make an independent assessment.

For high-purity paraxylene and benzene production, Jacobs found that renewably-sourced Bio-TCat products enable significant GHG reductions when compared to identical chemicals currently made from crude oil. Its LCA compared aromatics produced using loblolly pine feedstock from the southern US, to petro-aromatics produced in the US Gulf Coast from three crude oils which represented a range of carbon intensities. Their results for forest-to-gate found that CO_2 emissions for producing polymer-grade paraxylene and benzene from pulpwood using the process is estimated to be 70 – 80% lower than emissions for identical petro-based chemicals made from crude oils on a well-to-gate basis.

Figure 3. TCat-8 pilot plant.

Advantages for fuel blending

AnelloMate products, which are chemically identical to constituents found in conventional gasoline, will meet the criteria for 'cellulosic biofuels', defined by the Renewable Fuels Standard (RFS2) and US Environmental Protection Agency (EPA) as a fuel component produced from cellulose, hemicellulose, or lignin that delivers a 60% lifecycle reduction of GHG emissions.

The RFS2 regulations recognise that differences in energy density by fuel type are important. AnelloMate fuel blendstocks carry a higher RIN equivalence number of 1.5 D3 RINs/gal.

Table 1. Gasoline blending – intermediate and finished gasoline product properties (model refinery: 150 000 bpsd distillation capacity)

	Refinery gasoline BOB	AnelloMate hydrotreated C6	AnelloMate C7 – C9 heavy naphtha	Splash blended corn ethanol	Target specification	Final blend
Renewable content (vol.%)	0.00	100	100	100	10.00	10.00
Benzene (vol.%)	0.64	0.20	1.11	0.00	0.62	0.60
Sulfur (ppm)	10.40	0.00	1.00	10.00	10.00	10.00
RVP (psi)	7.40	3.30	0.40	30.60	9.00	9.00
Total olefins (vol.%)	12.10	0.00	0.00	0.00	10.50	10.90
Total aromatics (vol.%)	26.80	0.20	98.80	0.00	27.00	26.60
Octane (R+M)/2	85.00	78.00	109.00	113.00	87.00	87.00
Total volume (bpsd)	81 063	983	2223	5802		90 071
Blend (vol.%)	90.00	1.10	2.50	6.40		100
Annual RINs (millions)		23	51	89		163
RIN value at 2018 average prices (million US$)		54	121	41		216
RIN type		D3	D3	D6		

gasoline blendstock and 1.7 D7 RINs/gal. distillate blendstock compared to ethanol, which provides 1 RIN credit/gal. The additional credits provide greater value to refiners meeting their obligations, and are a bonus over ethanol produced by either conventional corn sugar fermentation or newer cellulosic feedstock processes.

Cellulosic biofuel blendstock from the Bio-TCat process offers refiners a new way to meet their fuel formulation obligations and take advantage of energy equivalence benefits. For example, a linear programme blending calculation was performed for a hypothetical refinery in the US with 150 000 bpsd crude distillation capacity, making 81 000 bpsd of blendstock for regular 87 octane (R+M)/2 gasoline with a requirement of 10 vol.% renewable content. The renewable content can be made with a combination of low-benzene C6 hydrogenated naphtha, C7-C9 renewable aromatic blendstock, and corn ethanol.

Table 1 shows the results of this calculation and indicates that 3.6% of the finished fuel contains renewable gasoline blendstocks and 6.4% contains corn ethanol for a total renewable content of 10 vol.%. The finished fuel meets all other specifications for benzene, sulfur, vapour pressure (RVP), olefins, aromatics, and octane. After accounting for RIN equivalence values, the Anellomate product provides 74 million RINs/yr and corn ethanol provides another 89 million. On a cost basis there are significant differences between cellulosic D3 RINs and conventional ethanol D6 RINs for gasoline. In 2018, the average price of a D3 RIN was US$2.37/gal. whereas the average price for a D6 RIN was US$0.46/gal. (according to the US EPA Moderated Transaction System database).[1] Using these prices, AnelloMate blendstocks provide US$175 million of RIN value compared to US$41 million for corn ethanol. If cellulosic ethanol is used instead of conventional, together with the naptha blendstock, the total blend value increases substantially. Having both corn ethanol and AnelloMate renewable fuel blendstocks available creates new blending options for refiners to better manage their renewable obligations, and the ability to offset other RVOs or to bank or trade the excess RINs is advantageous. If additional D3 RINs are desired, cellulosic ethanol may be used instead of corn ethanol.

Conclusion

Refiners need to find a new way to meet cellulosic biofuel requirements in order to add substantial flexibility to operations and logistics. The higher energy density of AnelloMate products, compared to corn ethanol, delivers more RINs/gal. blended, providing significant advantages to refiners and blending operators. A renewable blendstock and finished fuel, which is compatible with refinery blending systems, tankage, pipelines, and consumer vehicles, helps provide a reduction in GHG emissions for fuel use compared to petroleum-only routes.

Reference

1. US Environmental Protection Agency (EPA), 'RIN Trades and Price Information,' https://www.epa.gov/fuels-registration-reporting-and-compliance-help/rin-trades-and-price-information