

Delivering drop-in renewable fuels

A series of pretreatment, hydrotreating, and distillation steps converts fresh or used lipid based feedstocks to full range, drop-in renewable fuels

CHUCK RED and ED COPPOLA *Applied Research Associates*

ROBERT VALENTE, CHRISTINE CONWAY and LIN ZHOU *Chevron Lummus Global*

Hydrothermal Cleanup

Hydrothermal Cleanup (HCU) is a pretreatment step that uses traditional refinery components to remove inorganic materials from waste fat, oil, and grease feedstocks. During HCU, water is combined with feed oil and then fed to the HCU reactor system at the temperature and pressure necessary to maintain a hydrothermal/liquid-phase environment. Metals that are present in waste fats, oils, and greases (FOG) are mostly in the form of free salts and soaps. Phosphorus is mostly in the form of phospholipids. HCU relies on three primary mechanisms to achieve metals reduction:

- 1) Removal of soluble, free salts – similar to conventional desalting
- 2) Rapid acidulation of metal soaps (Na, K, Mg, Ca, Fe, others) using a weak acid
- 3) Hydrolysis of phospholipids into phosphate salts and phosphate-free lipids. Since oil and water are only partially soluble in each other at operating conditions, flow in the HCU reactor is maintained at a high Reynolds Number to achieve rapid mass transfer between each phase. Rapid mass transfer facilitates metals reduction by the mechanisms identified above.

Biofuels Isoconversion

The Biofuels Isoconversion (BIC) process converts freshly produced or used lipid based feedstocks, such as FOG into renewable fuels including diesel, jet, and naphtha. This process is unique because it produces fuels that are molecularly nearly identical to fuels produced from petroleum. The nearly identical chemistry results in jet and diesel fuels that are true 'drop-in'

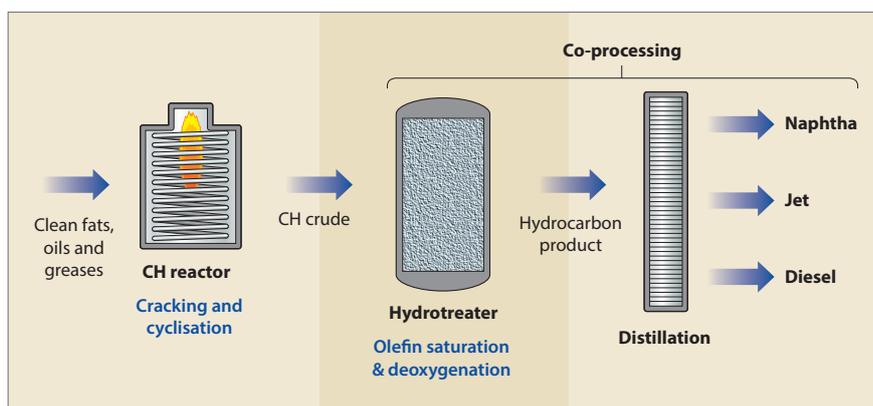


Figure 1 Simplified block flow diagram of the BIC process

fuels which do not require blending with petroleum. Therefore, the BIC process can be applied as an insertable unit to existing hydrotreating units which enables co-processing, or built as a stand-alone unit for renewable fuel production.

There are four main steps in the BIC process (see **Figure 1**): a cleanup step (HCU) where contaminants are chemically removed to make suitable feed oil for the next step; the conversion step, called catalytic hydrothermolysis (CH), wherein the feed oil molecules are converted to molecules that are nearly identical to those found in petroleum; a hydrotreating step that is identical to the petroleum hydrotreating processes that removes any remaining heteroatoms (oxygen, sulphur, nitrogen, and metals) down to acceptable levels; and a final distillation step that separates the hydro-treated product into the naphtha, jet, and diesel fuels.

Catalytic hydrothermolysis

In the CH process, water is combined with clean FOG products, pressurised, and heated in excess of supercritical water conditions. At these conditions, water and the

feed oil become one phase. Water mediates the conversion of free fatty acids into CH crude, containing compounds such as normal and branched paraffins, high-density cycloparaffins, and aromatic molecules ideal for diesel and aviation turbine fuels.

Key reactions that occur during CH conversion include, but are not limited to:

- Hydrolysis of glycerides to produce free fatty acids
- Cracking of fatty acids into lower molecular weight acids and hydrocarbons
- Cyclisation of fatty acids into alkyl cyclohexane compounds
- Cyclisation of fatty acids into alkyl benzene compounds
- Dehydrogenation of naphthenic compounds into aromatic compound,
- Decarboxylation of fatty acids
- Skeletal isomerisation of intermediate and product compounds

Typical CH reactions of unsaturated fatty acids, such as oleic acid and linolenic acid, are shown in **Figure 2**. Those reactions that occur in the CH unit eliminate the need for further catalytic reforming, hydroisomerisation, or hydroc-

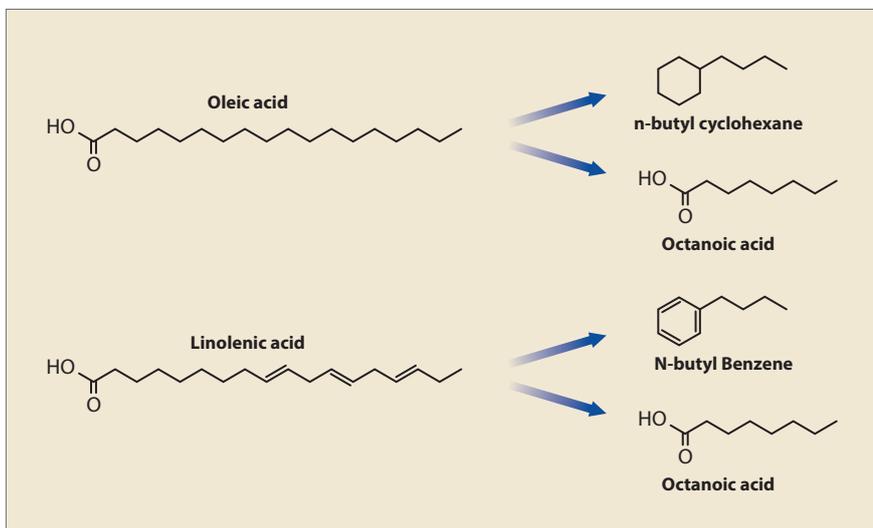


Figure 2 Characteristic CH conversion reactions

racking, and also consume less hydrogen than a route that uses all hydroprocessing.

The process occurs in a single step for less than two minutes of residence time. Product yields and product composition are controlled by adjusting the process variables, which include reaction temperature, reaction pressure, residence time, and water to oil ratio.

Isoconversion

The renewable CH crude contains oxygenated compounds, mainly carboxylic acids. In order to meet the fuel specifications, element oxygen must be removed from those oxygenates to produce pure hydrocarbons, and nearly all of the olefins must be saturated to produce paraffin compounds. For example, the total acid number (TAN, expressed as mg KOH/g) of jet fuel or jet fuel blending component under the CHJ Annex to D7566 must be less than 0.015. Hydrotreating achieves deoxygenation and reduces the TAN to meet the jet fuel specification. This results in jet fuel that has very good thermal and oxidative stability.

The BIC process uses commercial hydrotreating catalyst that results in near-complete oxygen removal (TAN <0.01) without saturating aromatic rings to cycloparaffins, opening cycloparaffin rings to form paraffins, or cracking of jet and diesel range hydrocarbons into naphtha and gaseous hydrocarbons. This results in fuels that contain aromatic and naphthenic

isomers similar in concentration and type to petroleum derived fuels. Because cycloparaffin and aromatic compounds are produced and retained in the products, the BIC process uses less hydrogen than hydrotreated esters and fatty acids (HEFA) type processes.

Product distillation

The BIC process produces the entire range of hydrocarbons from naphtha through diesel boiling ranges. To produce jet fuel, the whole hydrotreated product is distilled to meet several specification requirements that include distillation, distillation slope (T90-T50 and T90-T10), flash point, and freezing point.

BIC technology has features that overcome deficiencies with technologies that practise direct catalytic hydrogenation of triacylglycerides-rich feedstocks using fixed bed hydroprocessing catalysts. They include the following.

Unlike direct catalytic hydrogenation, which essentially converts triacylglycerides to their corresponding straight-chain n-alkanes (primarily high concentrations of n-hexadecane and n-octadecane), the BIC process incorporates cyclisation and aromatisation reaction chemistry to produce renewable jet and diesel fuels containing n-alkanes, isoalkanes, naphthenes, and aromatics, much more analogous to those in petroleum derived distillate fuels.

The catalytic hydrothermolysis reactor acts as a guard device to remove/transfer any inorganics

and potential hydroprocessing catalyst foulants into the aqueous phase product such that the downstream Isoconversion catalysts will sustain relatively longer catalyst lives.

Unlike direct catalytic hydrogenation, which converts the glyceryl backbone of the triacylglycerides to propane, and thereby results in consuming additional hydrogen, the BIC process converts the glyceryl backbone non-hydrogenatively into fuel gas for captive use in the CH reaction system.

Chemical hydrogen consumption in the BIC process is significantly lower than that in direct hydrogenation processes due to the supercritical water reforming of olefinic bonds in the unsaturated triglycerides via cyclisation and aromatisation reactions that produce lower hydrogen content naphthenes and aromatic hydrocarbons. By way of example, for a feedstock having a 13/1 unsaturates/saturates ratio, such as that in conventional rapeseed oil, the chemical hydrogen consumption for the direct hydrogenation route can be as high as 148% that of the BIC process.

In the production of jet fuels, aromatic content (ASTM D6379) is required to be 8-20 vol%. BIC technology produces aromatic rings, which enable drop-in jet fuel production independent of feedstock compositions.

A testing program carried out at Chevron Energy Technology Center in Richmond, California, has shown that the ReadiNaphtha can be catalytically reformed to produce reformate having a 98.8 RON and 87.3 MON (93 Anti-Knock Index) at a C₅+ reforming yield of about 70 vol%.

ASTM certification

ASTM D7566 Annex A6 has been approved to add a new standard for jet fuel (CHJ) produced by the Biofuels Isoconversion process. ASTM D7566 was developed by ASTM International (formerly the American Society for Testing and Materials) as an international standard for renewable jet fuel. Renewable jet fuel produced in compliance with the ASTM D7566 standard is deemed to meet the same require-

ments as those for conventional petroleum derived fuel, and thereby only renewable jet fuel produced and quality-controlled in compliance with this standard can be carried in commercial aircraft. The new annex allows the blending of up to 50% of ARA and CLG's Readijet with petroleum derived jet fuel.

Details of the new ASTM D7566 certification include:

- Date of issue: January 30, 2020
- Standards developing organisation: ASTM International
- Technology developing company: Applied Research Associates & Chevron Lummus Global
- Standard Number: ASTM D7566 – 19b (Annex A6 catalytic hydrothermolysis jet (CHJ))

Renewable oils co-feedstock component

Many feedstocks have been tested successfully in the CH conversion process since bench and pilot operations began in 2006. The CH process is tolerant of a wide range of renewable feedstock chemistries. Feedstocks may be highly saturated, such as tallow, or highly unsaturated, such as tung oil; they may contain esters with short chains, such as coconut oil (C₁₂), or long chains, such as rapeseed and carinata oil (C₂₂); they may be clean triglycerides or clean fatty acids. Feedstocks that have been successfully tested include waste oils, such as used cooking oil, tallow, and distillers corn oil, as well as virgin plant oils such as algae, camelina, canola, carinata, castor, coconut, corn (from distiller's grain), peanut, pongamia, soybean, and tung oil. More recently, work has been done that allows highly contaminated FOGs such as brown grease to be processed by pretreating with HCU. While feedstock chemistry affects conversion rates and product chemistry to a degree, the breadth of testing data enables CLG/ARA to provide sufficient process control to enable the production of jet and diesel fuels with consistent chemistry and quality.

Hydrotreaters

Renewable oils such as those from vegetable derived seed oils, non-edible plant oils, and animal fats are

characterised as hydrocarbonaceous oils containing:

- Three long-chain fatty acid molecules in the 12-24 carbon number range each connected to a glyceryl backbone
- Some unsaturated double bonds as non-aromatic olefins
- Some trace amounts of organic sulphur and organic nitrogen
- Some trace levels of metals such as Na, K, Ca, P, Fe, Mg

In the conventional direct hydrotreating process, these feedstocks are converted into a saturated and hydrodeoxygenated, mostly diesel range hydrocarbon mixture having essentially all straight-chain paraffins. Many literature references are showing that direct hydrotreating of renewable oils fails to meet diesel cold flow properties unless an expensive downstream selective isomerisation unit is installed. Therefore, the direct hydrotreated mixtures need further downstream catalytic hydrotreatment to significantly increase the isomer/normal paraffin to meet diesel fuel cold flow properties.

The CH step of the BIC process performs specific chemical reactions that generate not only iso olefins and iso-paraffins but also naphthenic and aromatic compounds in the CH crude oil derived co-feedstock component. This renders it much more like petroleum distillates than those of direct hydrogenated n-paraffinic rich renewable oils.

Some of the features of co-hydroprocessing renewable oils derived from the BIC pretreatment process with petroleum distillates include:

- HCU and CH reduce total metals content to less than 5 ppm, even for feedstocks with metals content starting at over 1000 ppm. This will allow co-processing of CH crude from renewable waste feedstocks without fouling the hydrotreating catalyst.
- Typical mid-distillate hydrotreating reactors can operate at a severity to simultaneously reduce the oxygen content of the renewable CH crude oil to less than about 10 ppm and the sulphur content of the petroleum compounds to less than 5 ppm.
- CH crude oil co-feedstock has a very attractive mix of hydrocarbon

types in the diesel precursor fraction that eliminates the requirement for expensive downstream selective isomerisation.

- Since most renewable oils are not available at volumes nearing nameplate capacities comparable to current petroleum hydroprocessing units, the co-hydroprocessing of blended petroleum/BIC partially treated crudes results in an advantageous economy of scale.
- Since hydrodeoxygenation of the BIC partially treated crudes produces water along with the hydrocarbon products, a water phase will be present in the recovery section to dissolve any ammonium sulphide produced from the hydrotreatment of the petroleum hetero-compounds to avoid potential solids deposition problems and without having to inject water externally.

Ebullated bed residue hydrocrackers

Recently, there has been interest in co-processing renewable oils and waste oils in an ebullated bed residue hydrocracker such as CLG's LC-Fining process. This co-processing option is generating much interest among refiners in Europe. As indicated above, the HCU process would be an excellent pretreatment step to remove impurities such as phosphorous and chlorides to a level that is acceptable to the catalyst and metallurgy of the unit. For this process, the CH step would be by-passed since the HCU oil will go directly into a hydrocracking environment.

Recently, the Environmental Protection Agency (EPA) enacted 40 CFR 80.1126, which allows for renewable oils to be co-processed with fossil derived oils in a petroleum refinery, with the renewable oil component qualifying for the Renewable Identification Number (RIN) programme.

Commercial development of the BIC process

ARA and CLG have advanced the commercialisation of BIC at a steady pace since its invention in 2006. ARA developed continuous flow bench and pilot systems in 2008 and 2010 and built a 100 b/d CH demonstration system in

2016, which was used to make over 160 000 gallons of 100% drop-in renewable jet and diesel fuels for US Navy MILSPEC certification testing in the F/A-18 Hornet and Spruance Class Destroyer.

The following are ongoing commercial activities for the BIC process:

- **Euglena:** a Japanese licensee recently completed the construction and start-up of an integrated demonstration system in Tokyo. The feedstock is a 30% algae (euglena) lipids/waste 70% palm oil mixture. The 5 b/d demonstration plant successfully produced Readijet and Readidiesel in early 2020.
- **Confidential Europe:** a commercial engineering study was completed to process 3900 b/d of rapeseed oil/animal tallow/used cooking oil.
- **ReadiFuels-Iowa (RFI):** a 2650 b/d commercial unit is currently in the final phases of basic engineering completion. Feedstock is 50% distiller's corn oil/50% used cooking oil.
- **Confidential USA 1:** a 5300 b/d commercial unit is scheduled to resume basic engineering activities soon. Feedstock is 50% yellow

grease/50% brown grease.

- **Confidential USA 2:** a 5000 b/d commercial unit's basic engineering activities are currently on hold. Feedstock is 60% yellow grease/40% brown grease.
- **Confidential USA 3:** a 3130 b/d commercial unit is currently in basic engineering. Feedstock is 50% distiller's corn oil/50% used cooking oil.

Biofuels ISOCONVERSION, Readinaphtha, Readidiesel and Readijet are marks of Applied Research Associates and Chevron Lummus Global. LC-FINING is a mark of Chevron Lummus Global.

Chuck Red is a Vice President with Applied Research Associates (ARA) and has led ARA's fuels programme since 2009. He has led the development and commercialisation of hydrothermal clean-up and catalytic hydrothermolysis technologies that produce 100% drop-in renewable jet and diesel fuel from waste fats, oils, and greases. He is a United States Naval Academy graduate with a BS in electrical engineering and holds MS in Business Management from Troy University.

Ed Coppola is a Principal Engineer with ARA where he directs research, development, test and engineering in alternative energy and renewable fuels development. He is a

co-inventor of the clean-up and conversion technologies employed in the Biofuels ISOCONVERSION (BIC) process. He holds a BS in chemical engineering from West Virginia University and MS in fuels engineering from the University of Utah.

Robert Valente is a Senior Principal Process Engineer with Chevron Lummus Global (CLG) in Bloomfield, New Jersey. With over 30 years' experience, his expertise is in biofuels, slurry hydrocracking, solid acid catalyst alkylation, LC-FINING, coking, visbreaking, styrene, selective CD-Hydro, and middle distillate hydrotreating. He holds a BS in chemical engineering from Manhattan College, New York.

Christine Conway is a Senior Principal Technology Specialist with CLG. With 20 years' experience working with refining and petrochemical technology licensing companies, she leads the development and design of the BIC technology. She holds a bachelor's degree in chemical engineering from the University of Minnesota.

Lin Zhou is a Process Engineer with Lummus Technology in Bloomfield, New Jersey, where she is responsible for the process design of CLG's BIC technology. With over 10 years of process engineering and R&D experience in biofuel production from bio-feedstocks, her research focuses on process intensification and catalyst formulation. She holds a PhD in chemical engineering from Stevens Institute of Technology, Hoboken, New Jersey.