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BIODIESEL ET HUILES HYDROTRAITÉES

Catalyst technology for biofuel production: Conversion of renewable lipids into biojet and biodiesel

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Abstract – Renewable lipids based biofuels are an important tool to address issues raised by policies put in place in order to reduce the dependence of transportation sector on fossil fuels and to promote the development of non-food based, sustainable and eco-friendly fuels. This paper presents the main features of the heterogeneous catalysis technologies Axens has developed for the production of biofuels from renewable lipids: the first by transesterification to produce fatty acid methyl esters or biodiesel and the second by hydrotreating to produce isoparaffinic hydroprocessed ester and fatty acids, high blending rate drop-in diesel and jet biofuels.

Keywords: Biofuels / renewable / fatty acid methyl ester / hydroprocessed esters and fatty acids / heterogeneous catalysis / Axens

Résumé – Technologie catalytique pour la production de biocarburants : conversion de matières grasses renouvelables en biojet et en biodiesel. Les biocarburants produits à partir de matières grasses renouvelables constituent un des principaux éléments de réponse aux problèmes posés par les réglementations en vigueur pour réduire la dépendance aux carburants fossiles dans les transports et pour promouvoir le développement de carburants à base de ressources non alimentaires, durables et respectueuses de l'environnement. Cet article présente les principales caractéristiques de deux procédés de catalyse hétérogène développés par Axens pour la transformation de matières grasses renouvelables en biocarburants : le premier par transesterification produisant des esters méthyliques d'acides gras ou biodiesel et le second par hydrotraitement produisant du biogazole et du biokérosène isoparaffiniques utilisables en grande proportion comme bases carburants.

Mots clés : Biocarburant / renouvelable / ester méthylique d'acide gras / acides gras et glycérides hydroprocessés / catalyse hétérogène / Axens

Introduction

Production of transportation fuels from renewable feedstock is one of the current major challenges. As transport sector is playing an important part in the increase of greenhouse gases emissions, it is essential to develop technologies reducing dependence on fossil resources for environmental reasons.

The development of biofuels has been promoted through incentive policies in many parts of the world. Europe is a good example: directive 2003/30/EC set targets for renewable energy share in transportation fuels at 2% in 2005 and 5.75% in 2010. The climate energy package directive 2009/28/EC targets, by 2020, a share of 20% of renewable energy in the EU energy end-use and a share of 10% of this type of energy in each member state in the transport sector. Sustainability criteria are also put in place in European legislation to encourage the use of resources that do not compete with the food chain and avoid undesirable effects such as deforestation or the use of environmentally sensitive land. Finally, objectives of GHG emissions reduction have been put in place for the biofuels: 35% GHG emissions saving by 2017 and 50% by 2018 for existing plants (commissioned before July 2014) and 60% GHG emissions saving for new plants (commissioned after July 2014).

Since early 90s, Axens has been a pioneer in the development and commercialization of technologies in order to address the challenges associated with the development of the biofuels sector. This paper presents the technological solutions proposed by Axens for the production of biojet and biodiesel from renewable lipids. Both are solid catalyst based technologies for production of middle distillates from renewable lipids: Esterfip-H^{TM} transesterification technology for fatty acid methyl esters (FAME) production and Vegan^{TM} hydrotreating technology for isoparaffinic hydroprocessed esters and fatty acids (HEFA) production. This latest technology has the advantage of producing hydrocarbon drop-in fuels

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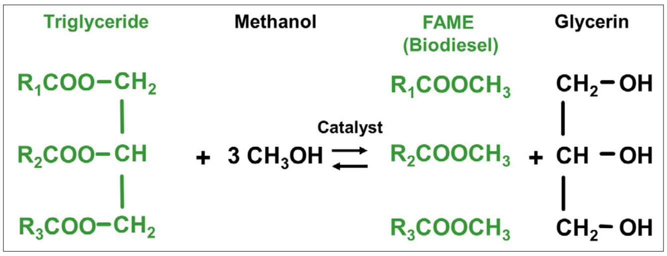

Fig. 1. Triglyceride transesterification reaction scheme.

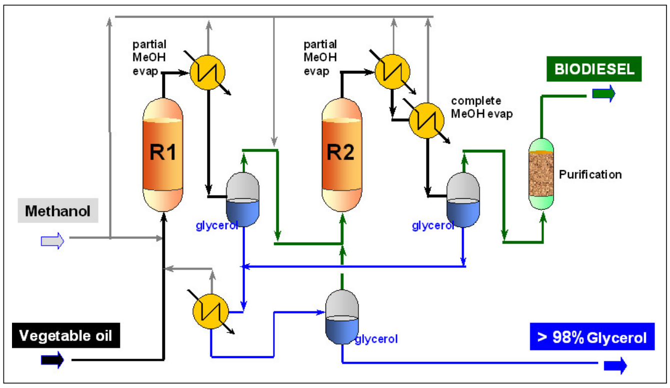

Fig. 2. Esterfip-H simplified process flow diagram.

Fig. 3. Diester Industrie Esterfip-H biodiesel facility in Sète, France.

having excellent qualities: high cetane number and adjustable cold flow properties allowing higher blending rates and their use as synthetic paraffinic kerosene blend stock for aviation fuel.

1 Esterfip-H technology

1.1 Transesterification reaction

The transesterification reaction of triglycerides to fatty acid methyl esters with methanol is a balanced reaction carried out in the presence of a catalyst (Fig. 1). An excess of methanol is required to obtain a high conversion. The FAME specification is defined by the EN14214 standard, which includes a minimum content of esters of 96.5% weight and maximum levels in mono, di and triglycerides (respectively 0.8%, 0.2% and 0.2% weight).

1.2 Esterfip-H solid catalyst technology

The Esterfip-H process, marketed by Axens, was developed by IFP Energies nouvelles and Axens (Bournay et al., 2005). This technology uses a heterogeneous catalyst composed of zinc oxide and alumina (Stern et al., 1999) used in extrudate form in fixed bed reactors.

The simplified process flow diagram of the Esterfip-H process is presented in Figure 2.

Conventional homogeneous catalyst transesterification process has several drawbacks: consumption of hazardous base and chemicals with associated operating cost and corrosion concern, low biodiesel yield with soap or low value fatty acid production and production of low grade glycerin containing high levels of salts and water.

The use of a solid catalyst allows an almost water-free process, avoids these disadvantages and as such, has many advantages in terms of economics (high biodiesel yield, low catalyst cost, high quality glycerin) and environmental impact.

In order to reach glycerides specifications in biodiesel, it is necessary to maximize the conversion and to shift the equilibrium of the transesterification reactions towards the formation of esters. This is achieved, on the one hand by using excess methanol and on the other hand by separating the glycerol formed during the reaction. To do this, the process consists of two reactors in series. These reactors contain a fixed bed catalyst and methanol and oil are injected up flow. Excess methanol is removed from first reactor effluent by partial evaporation and recycled, which improves glycerin separation from the effluent to be injected in the second reactor. The glycerin depleted effluent is injected with fresh methanol in the second reactor where the conversion of glycerides is completed to meet biodiesel specification. Methanol is completely evaporated from the second reactor effluent and recycled to the reactors, the glycerin is decanted, and the biodiesel then undergoes a final purification in order to meet glycerol specification. After methanol evaporation, glycerin product purity is higher than 98%, it typically contains less than 0.5% water (compared to 15–30% in the homogeneous process), it is also free of salts.

Sète plant in France was the first industrial plant using Esterfip-H. This unit is producing 200 kt/yr of biodiesel (Fig. 3). The design of the catalyst (geometry, chemistry, stability) allows it to operate at high throughput with a long lifetime which reduces the catalyst cost as compared to the homogeneous catalyst process. The somewhat lower activity of the catalyst is offset by operating conditions: temperature, pressure and excess methanol. However, suppression of waste production of low value fatty acids leads to a very high yield of ester per ton of oil, near to stoichiometric value.

Feed quality

Esterfip-H units process degummed, neutralized and dried oils. After crushing the seeds, the physical and solvent oil extraction, it contains around 100 ppm phosphorus mainly in the

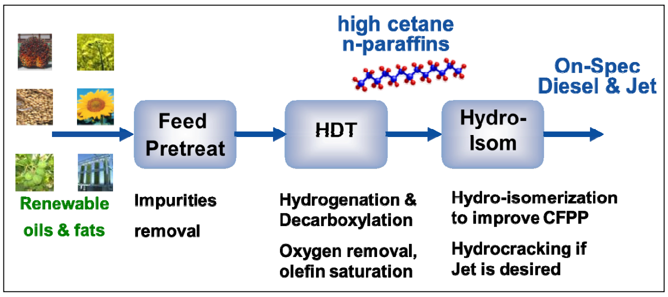

Fig. 4. Vegan^{TM} simplified block flow diagram.

form of phospholipids. However, the biodiesel specification requires a phosphorus content less than 4 ppm. The choice was made to remove these species prior to transesterification. Soluble phospholipids are simply extracted in water, non hydratable phospholipids are acid degummed to be solubilized in water. The oil is then neutralized to eliminate fatty acids formed by acid hydrolysis of a portion of the triglycerides and dried to remove residual traces of water.

Glycerin market

As already mentioned, one of the advantages of the heterogeneous catalyst Esterfip-H process is that it produces a high purity glycerin suitable without further processing for a large number of industrial users (glycerophtalic paints, polyols, etc.). Such glycerin is likely well adapted to the growing market of bio derived chemical intermediates (epichlorohydrin, lactic acid, etc).

Esterfip-H technology won the Kirkpatrick Chemical Engineering Achievement Award in 2007.

2 Vegan hydrotreatement technology

2.1 Drop-in fuels from renewable lipids

Although transesterification is widely used, methyl esters products contain oxygen and their fuel properties, including cetane number, cold flow properties and oxidation stability, remain highly dependent on the feedstock used for their production. These drawbacks limit their blending rates in diesel pool and even prohibit their use in cold climate regions and as aviation fuel blend stock.

To overcome these limitations, while taking advantage of renewable fats chemical structure similar to that of hydrocarbons of middle distillates cuts, Axens offers Vegan^{TM} an alternative hydroprocessing technology in order to produce completely deoxygenated, fully paraffinic, gasoil and kerosene with controlled fuel properties, fully compatible with fossil fuels (Fig. 4).

2.2 Hydrotreatment: getting the most out of lipids

The mechanism of hydrotreating of triglycerides is relatively complex and can be summarized with two main reaction pathways (Huber et al., 2007; Daudin and Chapus, 2009; Kubicka 2008) (Fig. 5):

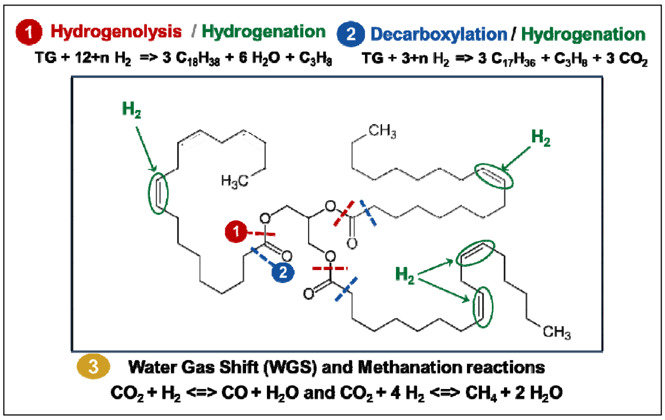

Fig. 5. Triglyceride hydrotreating main reaction scheme.

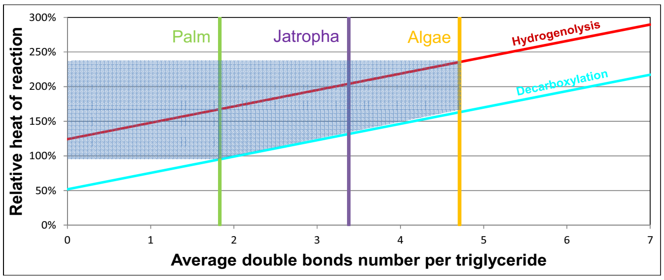

Fig. 6. Triglycerides hydrotreating exotherm.

- Hydrogenolysis (HDO), which leads to the formation of linear paraffins with the same number of carbons than in the initial fatty chains, along with the formation of water and propane.
- Decarboxylation (DCO), which leads to the formation of linear paraffins with a carbon less than the initial fatty chains accompanied by the formation carbon dioxide and propane.

Water gas shift and methanation also take place, yielding carbon monoxide and methane.

These main hydrodeoxygenation reactions are schematically represented below in the case of a C_{18} fatty acid triglyceride (n is the number of double bounds per triglyceride):

The challenges associated with this process are illustrated in Table 1 and Figure 6: potential variation of valuable paraffins yield with selectivity of reaction towards hydrogenolysis or decarboxylation and highly exothermic reactions along with important exotherm variation depending on feedstock slate.

These challenges are mastered in Vegan process through:

- A dedicated catalyst formulation based on Axens long term experience in promoted transition metal sulphide hydrotreatment catalyst which ensures optimum activity and selectivity.
- A novel reaction design in order to manage the heat release for an optimum temperature profile to control reaction selectivity and to limit catalyst deactivation.

Table 1. Theoretical yields of hydrotreating.

Feedstock	Rapeseed		Palm		Soybean	
Pathway	HDO	DCO	HDO	DCO	HDO	DCO
H2 consumption, wt% feed	3.6	1.5	3.2	1.2	3.8	1.7
Paraffins yield, wt% feed	86.3	81.5	85.3	80.4	86.4	81.6
Propane yield, wt% feed	5.0		5.2		5.0	
H_2O yield, wt% feed	12.3	–	12.7	–	12.4	–
CO_2 yield, wt% feed	–	15.0	–	15.6	–	15.1

Table 2. Melting point and cetane number of linear paraffins.

Paraffin	Melting point, °C	Cetane number
n-C12	–10	80
n-C14	6	95
n-C16	16	100
n-C18	28	106

2.3 Hydroisomerization: producing high quality fuels

Normal paraffins or waxes produced by hydrotreating of renewable lipids exhibit high cetane number but poor cold flow properties (NIST Database; Murphy et al., 2004; Daudin et al., 2012) (Table 2). As compared, EN590 European gasoil standard Cold Filter Plugging Point specification ranges from +5 °C to −45 °C depending on season and climate. These paraffins can, therefore, be used only at low blending rates in diesel pool (if a low blending rate is targeted, co-processing of lipids in existing diesel hydrotreating units will be preferred).

For the production of diesel with appropriate cold flow properties, these linear paraffins must ideally be transformed into molecules of identical composition but with a branched chain via an isomerization reaction. Cetane number is slightly affected but remains high. A high isomerization rate is accompanied by a risk of rupture of the carbon chain or hydrocracking. The choice of the catalyst and the operating conditions of the hydroisomerization must therefore be optimized so as to lead to the best compromise between yield and cold flow properties.

When jet fuel is targeted, higher severity is applied to produce highly branched isoparaffins along with hydrocracking in order to meet both boiling range and freezing point specifications.

The Vegan hydroisomerization technology has been developed based on Axens' long experience in conventional fixed bed hydrocracking and hydrotreating of various refinery feedstock. A dedicated catalyst has been developed for hydroisomerisation and hydrocraking of the Vegan HDT normal paraffins, giving Vegan technology the versatility to produce tailored diesel blendstock and ASTM D7566 compliant HEFA biojet.

Conclusion

Esterfip-H has proven its effectiveness for the production of biodiesel (FAME) with high quality glycerin, proposing a smart solution to the main drawbacks of the conventional homogeneous process. When high quality, drop-in biofuels from renewable lipids are expected, then the production of HEFAs can be the right choice and Vegan^{TM} the right hydrotreating technology. This flexible two-step process has the advantage of producing tunable grade diesel as well as biokerosene drop-in fuels almost independently from the feedstock quality, thus opening new horizons of development both for road and air transport (commercial or military). It has also the advantage of being a process close to conventional hydrotreating processes which the refiners are more familiar with and easier to integrate in a refinery. Its commercial deployment shall be boosted in the next decade by the development of new non-edible, sustainable and affordable lipids feedstock.

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