Stanka Leskovac, Ivan Souček, Vladimir Koprivšek, Martin Kubu

ISSN 0350-350X
GOMABN 54, 2, 138-148
Professional paper

POSSIBILITY FOR REFINERY NOVI SAD UNITS RECONSTRUCTION FOR HYDROGENATED VEGETABLE OIL PRODUCTION

Abstract

The aim of the project is to design and construct the processing unit including necessary logistic facility capable to treat vegetable oils, sludge from eatable oils production, used cooking oil for production of renewable diesel (RD) component – hydrogenated vegetable oil (HVO). HVO meets CEN Technical Specification TS 15940:2012 [1] for paraffinic diesel thus may be blended into diesel fuel without any limit (except density); no special labeling at fuel retail stations is required. The proposal emphasizes the usage of the existing refining technology for proposed HVO production process, maximizing usage possibility of the existing units and/or equipment in Novi Sad refinery. The plant of 150 000 t/y has been considered, with hydro-treatment and hydro-isomerization as the two main processing units, with distillation section at its end maximizing renewable diesel production. This production also provides approx. 37 500 t/y of valuable by-products (bio-C1/C2, bio-LPG, bio-naphtha, bio-jet). The technology evaluation shows that the viability of the HVO project is strongly dependent on the availability of raw materials, their prices and purchase conditions.

***Key words**: HVO - hydrotreated vegetable oil, renewable diesel, green refinery*

Introduction

Bioenergy has historically been a major component of the whole renewable energy generation volume in the world. After the '70s oil crisis and later in '90s in relation to the increase of the CO_2 and GHGs in the atmosphere, the interest in renewable energy technologies and bioenergy in particular for transport has rapidly increased [2-4]. This article provides an overview of a possible production using existing equipment of Refinery Novi Sad (RNS); describes the HVO/RD production process, feedstock used, yield and product quality, discusses the compatibility of HVO/RD with existing petroleum fuels infrastructure and vehicles; assesses the potential market penetration of HVO/RD in the SEE region and other market factors such as existing and predicted supply and demand for HVO/RD, renewable fuels regulations and incentives and fuel prices as an opportunity. The bio-based vegetable oils and/or animal fats technologies for production of biodiesel and renewable diesel are and will ultimately be challenged by two basic obstacles relative to petroleum:

1. economics and
2. performance linked with characteristics of these fuels comparative to mineral oil products.

The first challenge relates to the simple question: is the bio-based product or technology cost competitive with traditional petroleum based feedstock or related technological processes? In general, as petroleum prices rise, the easier it was to justify substituting a crude oil feedstock with a bio-based vegetable seeds oils and/or animal fats feedstock. As petroleum prices fall the inverse is true, bio-based feedstock face inflection points in pricing where they become more costly relative to petroleum. The periods of record high prices of crude above 110-130 USD/barrel are providing significant opportunities for bio-based products to gain interest from those manufactures that were looking to replace their high cost oil feedstock. It was identified [5-7] that break-even price of crude oil in respect to mineral vs. renewable diesel is about 130 USD/bbl.

The second question relates to how well the respective bio-based product or technology performs relative to traditional petroleum manufacturing platforms. The growth of bio-based products and technologies has not been confined to only the large fuel markets and market players. Significant advancements have occurred in numerous other markets because of the desirable environmental properties of renewability and biodegradability. These attractive properties are creating new and exciting opportunities for feedstock that are based on vegetable seeds and/or animal fats. On the supply side, the pace of introduction of renewable fuels depends not only on the availability of the feedstock and fuels but also on the compatibility of the supply and distribution system for all fuel products (including proliferation of blending options). But, the main condition of larger use of renewable diesel is price of crude oil and respective pricing of mineral vs. renewable products.

Hydrogenated vegetable oil - HVO

Renewable diesel or HVO is defined as "any of several diesel substitutes produced from renewable feedstock that chemically are not esters and thus are distinct from biodiesel" (definition by Renewable Diesel Subcommittee in the United States [8]).

The HVO/RD, due to its chemical composition, is a mix of pure paraffin, linear and branched, in different proportions as related to the degree of isomerization required. It is an optimum bio-component for blending. The high-quality renewable diesel can provide higher heating values and energy density than that of FAME [9]. Result is that less renewable diesel is required to satisfy the same bio-mandate. HVO is:

- explicitly mentioned by both the RED [9] and the FQD [10] directives;
- by definition is not biodiesel (only FAME is classified as biodiesel [11]);
- meets compositional requirements set by FQD Annex II [10] for diesel fuels;
- has hydrocarbon nature according to FQD recital 33 [10];

- meets TS 15940 [1] specification of paraffinic diesel fuels for dedicated vehicles;
- may be blended in Europe according EN 590 [12] and in USA according ASTM D 975 [13] without any limit ("blending wall") or labeling at fuel retail stations;
- energy content is defined in RED Annex III [9];
- typical and default greenhouse gas values are defined in RED Annex V [9] and FQD Annex IV [10];
- amount of HVO in diesel fuel blend can be estimated by radioisotope carbon C14 method [14].

HVO is the real "drop-in" fuel, having the excellent properties which help minimize:

- blending costs by making it possible to fulfill the entire biofuel mandate at the most cost-effective blending locations;
- logistics costs by making it possible to use existing diesel logistics;
- impact on refinery output by optimizing diesel production with a low-density, high-cetane blend-stock component.

Table 1: Properties of ULSD, BIODIESEL and HVO/RD [15]

Property	**ULSD**	**FAME**	**HVO**
Carbon, wt%	86.8	76.2	84.9
Hydrogen, wt%	13.2	12.6	15.1
Oxygen, wt%	0	11.2	0
Specific Gravity, kg/m^3	850	880	780
Cetane No.	51-55	45-55	70-90
T90, °C	300-330	330-330	290-300
Viscosity, mm^2/s @ 40 °C	2-3	4-5	3-4
Energy Content (LHV), MJ/kg	43	37	44

The very high cetane number and optimum cold flow properties (CFPs) are attainable due to the isomerization stage of the hydroprocessing. In addition, the renewable diesel is of lower density making it an excellent blending component for refiners limited in using heavy gasoil in diesel blending. Addressing the minimum density limit for EN 590 [12] EURO 5 diesel fuel specifications, the maximum amount of renewable diesel in the blend could be about 30 vol%. Furthermore, the low aromatics content is an additional benefit when blending with other petroleum diesel products. Another advantage when compared against FAME is that the renewable diesel has the same behavior as the fossil-based diesel regarding storage and logistics. Currently, there are no fuel standards that have been developed uniquely for HVO/RD, neat or blended. HVO/RD is comprised of the same types of hydrocarbons as conventional diesel and therefore is subject to the same fuel standards as ULSD: CGSB 3.517 in Canada [16], ASTM D975 in the United States and EN 590 in Europe. Since HVO/RD is a fuel that is fully fungible with ULSD, infrastructure requirements for blending HVO/RD with ULSD are minimal and are mostly related to inventory management. No significant vehicle equipment compatibility issues have been found either.

The additional benefit for refiners is based on the fact that heavier and lower-cetane diesel cuts can be produced adjusting the crude distillation or by upgrading FCC light cycle oils into the diesel pool. In terms of refinery economics, these no-CAPEX improvements often result in significant financial benefits. By switching its biofuel component from 7% conventional biodiesel to 30% low-density HVO/RD, a refinery can produce up to 3.7% heavier diesel cut. HVO/RD can be produced from virtually any type of bio-based renewable feedstock. The most common feedstock is vegetable oils and animal fats, which are made up mostly of triglycerides and are types of feedstock that is traditionally used for biodiesel production. However, HVO/RD can be produced from a wider range of feedstock than biodiesel, incl. bio-wastes like residue from vegetable oils storage, i.e. sludge.

Table 2: Global HVO/co-processing outlook details [17]

Production plant	Capacity (KTA)
Neste Oil Porvoo, Finland (HVO)	380
Neste Oil Rotterdam, Holland (HVO)	800
Neste Oil Singapore (HVO)	800
ENI/UOP, Livorno*, Italy (HVO)	500
GalpEnergia, Portugal	250
PREEM Oil, Sweden (co-processing)	100
UPM, Finland (biorefinery)	100
Diamond green diesel, USA (HVO)	450
Emerald biofuels, USA (HVO)	250
Dynamic Fuels LLC, USA (HVO)	270
Additional HVO/ co-processing (EU)	510
TOTAL (EU sites only)	**2 640**
TOTAL (Global)	**4 410**

** The project transferred from Livorno to Venice “Green” refinery with capacity 300 KTA [18]*

The advantage of the HVO/RD production process is that it makes use of existing refining technology. Hydrotreatment units are already used in conventional refineries in order to desulfurise distillate fractions, including diesel oil.

As such, this same technology can be applied to the hydrotreatment of vegetable oils to produce HVO/RD taking into the consideration specific design conditions required by applicable technologies. There are several plants for HVO production already in operation and/or being built in Europe, USA and Singapore (Neste Oil, Eni, Diamond Green Diesel, Dynamic Fuels LLC etc.) totaling approx. 4.7 mil tonnes of HVO and/or HVO/mineral diesel co-processing annual capacity.

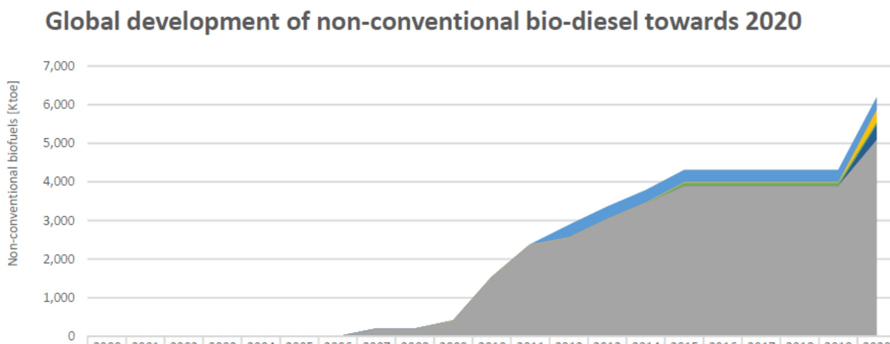
The first renewable diesel production pathway, renewable diesel I, was modeled after a process called Super Cetane that was originally developed in the 1980s at the Saskatchewan Research Council. The second renewable diesel production pathway, renewable diesel II, or Green Diesel was modeled on a hydrogenation process developed in cooperation between Eni and UOP, a Honeywell Company (production scale unit is now under construction in Eni refinery Venice). The different but still the third pathway in production of renewable diesel “Catalytic Hydrothermolysis” (CH) developed in 2006 was modeled on a hydrothermal process wherein supercritical water catalyzes the CH reaction of triacylglycerides (TAG) to form free fatty acids (FFA) and hydrocarbons under patent of ARA US (Applied Research Associates - ARA), followed by iso-conversion process which converts FFA to n-paraffins (proprietary technology by Chevron Lummus Global).

A number of technology providers-licensors around the world have developed HVO/RD processes and are now producing commercial volumes or are at the beginning of constructing commercial facilities: Neste Ool (NExBTL), Axens (VEGAN), Chevron (BIS-Biofuel Iso-conversion Process), UOP/Eni (ECOFINING), Syntroleum (Biofining), Haldor Topsoe (Hydroflex), Petrobras (H-BIO). Neste Oil is the refiner that currently operates a number of a renewable diesel units: at its Porvoo oil refinery in Finland, with a production capacity of 170 KTA (2007); second NExBTL plant (2010) at Porvoo (210 KTA), a third unit in Singapore (800 KTA) in 2010 and the fourth Neste plant in Rotterdam with the capacity of an 800 KTA in 2011 [19]. NExBTL's raw materials include palm oil, rapeseed oil, and animal fats. Neste Oil is followed in Europe recently by Italian Eni which is reconstructing former oil refinery to bio-refinery.

The Eni Venice Green Refinery Project is a highly innovative idea which will transform the traditional concept of the refinery into a "green" cycle, for the production of high quality bio-fuels from oil biomass at low cost, thanks to an investment of about 100 million euro [18]. The project involves the conversion of existing units, used, until a few months ago, for the production of fuels from crude oil, thanks to the application of the ECOFINING technology, designed and developed by eni in conjunction with the company UOP. The biorefinery that will be operating in Venice responds to the need of adding components of “organic“ origin to conventional fuels to satisfy the prescriptions of the European Directives. Such need allows eni to supply almost 1 million tons of bio-fuels (FAME, ethanol and bio-ETBE) currently entirely purchased on the market. Thanks to the Green Refinery, the Venice production site will produce around 50% of the bio-fuels needed from Eni to satisfy the RED 20-20-20 policy.

The main product of the Venice bio-refinery is Green Diesel, and it will take place of the FAME biodiesel in Eni's fuel. It is obvious that similar movements are expected in another European region, including possibly Serbia.

The increase of global non-conventional biofuels availability in 2020 is expected, mostly based on increase in non-conventional bio-diesel caused by HVO/co-processing projects. Even though there are almost no definite announced start-up year, JEC in its study [17] assumed that these projects will be operational before 2020 and for calculative purposes the start-up year is set on 2020. It remains to be seen whether all projects will be implemented.



	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020
Biodiesel other	0	0	0	0	0	0	0	0	0	0	0	0	316	316	316	316	316	316	316	316	316
DME Waste Wood	0	0	0	0	0	0	0	0	0	1	1	2	2	2	2	2	2	2	2	2	2
Biodiesel Waste Veg./AF	0	0	0	0	0	0	0	0	0	14	14	14	14	14	14	14	14	14	14	14	311
Biodiesel FT Farmed Wood	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	71	71	71	71	71	71
Biodiesel Waste Wood FT	1	1	1	1	2	2	2	2	2	2	2	2	2	3	3	3	3	3	3	3	397
HVO/Co-processing	0	0	0	0	0	0	0	200	200	400	1,524	2,366	2,555	3,028	3,449	3,904	3,904	3,904	3,904	3,904	5,092

Figure 1: Global development of non-conventional bio-diesel towards 2020 [17]

NIS - possibility for HVO production (RNS as a "green refinery")

During UN sanctions Serbia was one of the pioneers in European Biodiesel Sector. The highest level of production was achieved in 2007. Today, production and consumption are on symbolic level. Obligations towards Energy Community dictate that by the end of 2020 Serbia has to fulfill 10% e.e. of biofuels in transport sector. Because of EN 590 constrains, other renewable diesel components will be required. Using only FAME, oil companies in Serbia will be able to fulfill only 5.2% e.e. Based on predicted consumption it is estimated that in 2020 Serbia will consume >150,000 tons of biodiesel / HVO. There is over 100 KTA of FAME production capacities in Serbia (which is currently not being used due to the absence of obligation and better economy for edible oil production), but no other technology for renewable diesel production in place.

NIS RNS refinery could be converted to „green refinery“ and become NIS production center for renewable fuels, producing bio-based LPG, naphtha, jet and diesel (via process of hydrogenation of vegetable oils and/or co-processing with mineral diesel) and the 2nd generation bio-ethanol, produced from ligno-cellulosic sources (bio-mass, e.g. residual non-food parts of crops like stems, leaves and industry waste such as woodchips) in partnership with domestic suppliers, using new and existing refinery units (e.g. for diesel hydro desulfurization), utility systems and infrastructure.

Applicability of HVO technology in Novi Sad refinery

The first step in the HVO/RD production is hydroprocessing of vegetable oil where triglycerides are reacting with hydrogen to form primary product of n-alkanes, CO_2 and propane. This process occurs within hydrotreating, decarboxylation and hydro-cracking steps. Production plant usually consists additionally of isomerization unit which is used to isomerize hydrotreated vegetable oil. In the second reactor, the mixture is isomerized, under hydrogen partial pressure over proprietary catalyst. The linear paraffin chains are branched to improve cold-flow properties of the final products. A typical refinery distillation train is used to separate the array of product components and to obtain LPG, Jet, Naphtha and Diesel.

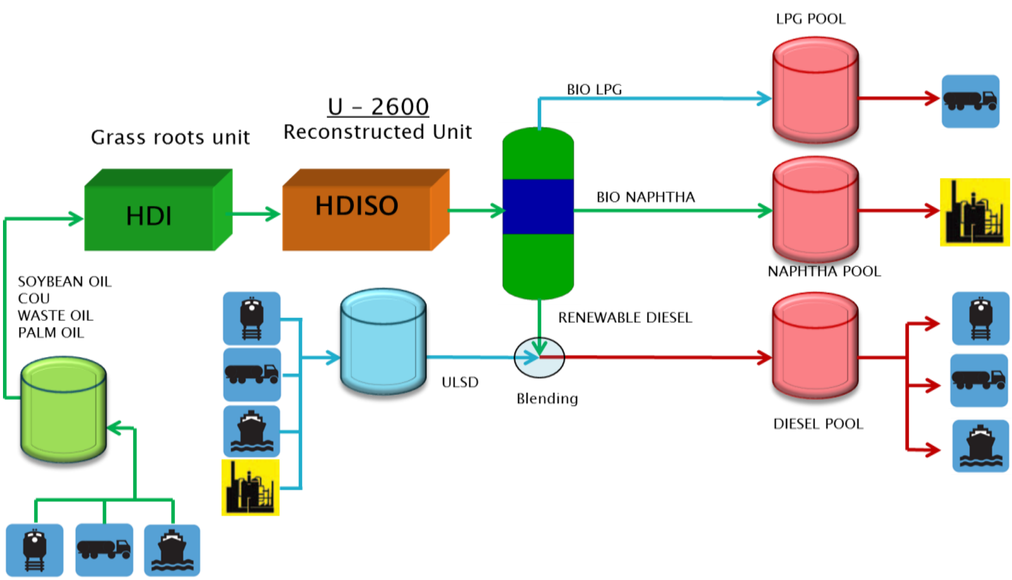


Figure 2: Proposed flow scheme for HVO production

After evaluation of suitability of existing equipment of Novi Sad refinery which is not recently in utilization, it is considered that some equipment could be utilized but some key equipment (referring to existing technological options) should be installed as new:

- One of HDT reactor could be used for one of stages of HVO process but one new should be added.
- Concerning the fractionation section, HP stripper and all the associated equipment can also be reused but existing LP stripper cannot be used and a new splitter with re- boiler is required.
- Some other off-sites equipment.

The HVO/RD new equipment would be located adjacent to the existing units, which would allow for integration with existing support and utilities. The facility could be well integrated to maximize efficiency and utilize infrastructure already in place, thereby significantly reducing impact of project CAPEX. The integration would require the construction of several tie-ins from / to existing infrastructure. The HVO/ RD project would receive power from the existing substation located adjacent.

The plant capacity of 150 KTA HVO has been considered based mainly on soybean refined oil as raw material. It was considered to have readily available the following quantities of vegetable feedstock in amount of 137 KTA from domestic sources (the remaining feedstock, 70 - 80 KTA, needs to be imported):

- 130 KTA of vegetable oil;
- 5 KTA of used cooking oil (UCO);
- 2 KTA of edible tank oily waste sludge.

Table 3: Rape seed and soy bean production in Serbia (2009-2013) [20]

	Rape seed			Soy		
	Harvested area, ha	**Total yield, t**	**Oil yield, 38-45% (41.5%)**	**Harvested area, ha**	**Total yield, t**	**Oil yield, 14-25% (19.5%)**
2009	18091	44300	**18385**	144386	349193	**68093**
2010	12012	24399	**10126**	170255	540859	**105468**
2011	15357	44531	**18480**	165253	440847	**85965**
2012	8258	20076	**8332**	162714	280638	**54724**
2013	9686	26992	**11202**	159724	385214	**75117**

Feedstock

The main feedstock foreseen for the purpose of HVO production in Novi Sad refinery is vegetable oil based on refined soybeans oil. The process is also supposed to utilize UCO and/or edible oil tank sludge up to the amount of max. 15% of the total feed (recognizing that collection of UCO is the main issue not only in Serbia but also in whole EU). Today's, as per the official reports, collectible potential for UCO in Serbia is definitely lower than 6.5 KTA. In further evaluations of the planned project viability, we have adopted a more realistic assessment that from domestic "waste sector" about 5.0 KTA of UCO might be provided, but even these limited quantities only with very well organized activities on collection.

Second possible feedstock in category of waste materials is oil sludge, so-called „soap stocks“ 4.0 KTA resulting from aging of crude vegetable oil in storage tanks and from vegetable oil factories equipment cleaning. It was supposed that 50% are to be used for HVO production.

In the future other non-food bio-based material should be considered as the raw material input, animal and rendering fats being the most important alternative. The main source of the raw material shall be from domestic vegetable oil production. But as we have discovered Serbia does not have enough oil plants available and certain actions should be done.

Prices

The Project is most sensitive to changes in the prices of final products and direct material inputs, i.e. the price of HVO and the price of pre-refined vegetable oil, respectively. Namely, the share of HVO's sales in total revenues is over 80% in all the scenarios, and the share of major vegetable oil (soybean oil or/and palm oil) in total cost of feedstock is 95-97% or in overall operating costs about 90%. The project is least sensitive to volume of production (or in other words, to dimension of designed capacity to produce HVO).

Conclusions

Several key conclusions as a result of the economic analysis are summarized as follows:

1. In the mid-term horizon the profitability of the Project is extremely tight. It seems that in next 7-8 years such kind of Project might be viable only in presence of Government incentives within a sustainable biofuel policy and Serbia's overall attempts to reach "EU 2020 targets" (budgetary support in terms of tax exemptions and excise reduction, or eventually subsidies although it is unlikely).

2. When the Project is analyzed as a future entity integrated within NIS a.d. core business system as interactively linked to the functioning of the parent company, and when indirect effects that the Project might have to a total business activities of NIS a.d. are estimated and taken in the account, then project from its very beginning indicates excellent viability of financial and economic performance.

3. In long-term horizon there is a real chance that the project will become commercially viable, and that its profitability will raise continuously, due to two main reasons:

- difference in prices of petroleum derivatives and vegetable oils is expected to be continuously increased since the first group of products are based on limited fossil resources and the second group of products are based on renewable resources
- price of vegetable oils are expected to go down, as a consequence of latest EU Directive which limits use of first-generation biofuels in Europe, which will automatically impacted the global market of vegetable oils.

4. By introduction of this product, up to 50% of CO_2 savings can be achieved (comparing to mineral diesel consumption).

References

1. *CEN Technical specification TS 15940:2012*
2. *ConocoPhillips Begins Production of Renewable Diesel Fuel at Whitegate Refinery in Cork, Ireland*. Press release, December 19, 2006
3. Ostrovski N.: "*Zeleni dizel" kao alternativa "Biodizelu",* Zlatibor, Energetika, 2010
4. UOP for U.S. Department of Energy: *Opportunities for biorenewables in oil refineries;* Final technical report; 2005
5. Souček I., Ocič O.: *Long-term sustainability of bio-components production*, Hemijska industrija, 66(2):235-242, 2012
6. Souček J., Souček I.: *Směry zvýšení efektivnosti výroby biopaliv*, Paliva 3, 2011
7. Souček I., Popovič Z., Koprivsek V., Leskovac S., Ocič O., Kubu M.: *Alternative bio - diesel production, conference Energetika,* Zlatibor, 2014
8. Brady At al: *Renewable Diesel Subcommittee*, USA, 2002
9. *Directive on Renewable Energy Sources (RED)*, European Norm 2009/28/EC
10. *Directive on Fuel Quality Standards (FQD)*, European Norm 2009/30/EC
11. *European Norm for bio-diesel*, EN 14214
12. *European Norm for Diesel*, EN 590
13. *US Norm for Diesel, ASTM D 975: Standard Specification for Diesel Fuel Oils*
14. Argonne National Laboratory: *Life-Cycle Assessment of Energy and Greenhouse Gas Effects of Soybean-Derived Biodiesel and Renewable Fuels*, March 12, 2008
15. Hoekman S. K., Gertler A. W., Broch A., and Robbins C.: *Investigation of Biodistillates as Potential Blendstocks for Transportation Fuels.* Desert Research Institute, CRC Project number AVFL-17, June 2009
16. *Canadian Norm for Diesel, CG SB 3.517*
17. EU Commision, JEC Biofuels Programme 2013.: *EU renewable energy targets in 2020: Revised analysis of scenarios for transport fuels,* May 2014
18. Rispoli G., Amoroso A., Prati C.: *Venice's Biorefinery: How refining overcapacity can become an opportunity with innovative ideas,* Hydrocarbon Processing (HPI Focus), February 2013.
19. Mikkonen S.: *Second-generation renewable diesel offers advantages*. Hydrocarbon Processing, 87(2008) 2, p. 63-66
20. Statistical Office of the Republic of Serbia: *Statistical Office databases*

Abbreviations

BTL Biomass-to-Liquid
UCO Used cooking oil (waste cooking oil)
e.e. Energy Equivalent
FT Fisher/Tropsch process
(applied for Gas-to-Liquid or Biomass-to-Liquid processes)
GHG Greenhouse gases
FAME Fatty Acid Methyl Esters
HVO Hydrogenated vegetable oil

HDS Hydrodesulphurization
KTA thousand tons per year
RNS Novi Sad Oil Refinery
RD Renewable diesel
RME Rapeseed Methyl Ester
SEE South East Europe
t/y tons per year
ULSD Ultra-low sulphur diesel

MOGUĆNOST REKONSTRUKCIJE POSTROJENJA U RAFINERIJI NOVI SAD ZA PROIZVODNJU HIDROGENIZIRANOG BILJNOG ULJA

Sažetak

Cilj projekta je osmisliti i izgraditi procesno postrojenje, uključujući i neophodnu logističku opremu, pomoću koje će se moći preraditi biljna ulja, ostatak proizvodnje jestivih ulja, korištena jestiva ulja, a za proizvodnju obnovljive komponente za dizel – hidrogenizirano biljno ulje (HBU). HBU zadovoljava CEN tehničku specifikaciju TS 15940:2012 za parafinske dizele, te stoga može biti namiješan u dizelsko gorivo bez ograničenja (osim gustoće); posebno označavanje na benzinskim postajama nije potrebno. Prijedlog potiče korištenje postojeće rafinerijske tehnologije budući da predloženi proces za proizvodnju HBU maksimizira korištenje postojećih postrojenja i/ili opreme u rafineriji Novi Sad. Razmatrano je postrojenje kapaciteta 150000 t/g s hidroobradbom i hidroizomerizacijom kao glavnim procesnim jedinicama i sekcijom za destilaciju na kraju procesa, u cilju maksimalne proizvodnje obnovljivog dizela. Ova proizvodnja također osigurava i oko 37500 t/g vrijednih nusproizvoda (bio-primarni benzin, -UNP, -C1-C2). Procjena tehnologije pokazala je da isplativost HBU projekta jako ovisi od raspoloživosti sirovina, njihovoj cijeni i uvjetima nabave.

Authors

Ing. Stanka Leskovac, NIS a.d., Republic of Serbia; e-mail: stanka.leskovac@nis.eu
Ing. Ivan Souček, Ph.D., VŠCHT Praha, Czech Republic
Ing. Vladimir Koprivšek, NIS a.d., Republic of Serbia
Ing. Martin Kubu, Agrofert, Czech Republic

Received

14.10.2014.

Accepted

11.11.2014.