DEVELOPMENT OF A SECOND-GENERATION NAPHTHENIC DROP-IN FUEL FOR SPARK IGNITION APPLICATIONS

T. Robeyn*, T. Larsson*, S. Verhelst*
tom.robeyn@ugent.be
*Ghent University
Research Group STFES (Sustainable Thermo-Fluid Energy Systems)
Sint-Pietersnieuwstraat 41
B-9000 Gent, Belgium

Abstract
Second-generation (2G) biofuels are one of the pathways to sustainable mobility. Not relying on feedstock or land use for food production, these types of biofuels offer advantages over their first-generation (1G) counterparts. However, the production techniques involved present considerable challenges on a technical and an economical level. A novel 2G biofuel production technique has been designed in an effort to overcome these challenges. Based on a catalytic process that operates at low temperature, it converts woody biomass feedstock into a stable light naphtha. The process development is integrated in the Belgian federal government funded Ad-Libio project (short for "Advanced Liquid Biofuels"). The process outcome mainly consists of hydrocarbons containing five to six carbon atoms. The ultimate goal is to produce a drop-in fuel that can be fully interchanged with the gasoline fuels in use today. Since the Ad-Libio fuel components differ significantly from gasoline fuel components, the suitability of several blends of these components needs to be investigated. To that end, a fuel blend calculator with integrated fuel database has been developed. Enabling fast SI fuel property calculations, the tool is used to make quick decisions on the fuel production process outcome. This allows modification of the production process so that only promising fuel blends are generated. Verification of the fuel blend calculations were then performed in the lab by means of a simplified octane verification method. Finally, the most promising fuel blend was sent to an ASTM-compliant laboratory for Research Octane Number (RON), Motor Octane Number (MON) and Reid Vapor Pressure (RvP) evaluation, confirming the promising results from the fuel blend calculator. This article describes the calculation and verification methodology of the blends that are generated by the novel production process, ultimately aiming for a sustainable second-generation drop-in gasoline fuel replacement.

The importance of biofuels

Germany's FVV's Future Fuels Study IV [1] states that, when assuming that a fully defossilized energy/fuel supply is achieved by 2050, cumulative greenhouse gas (GHG) emissions are dominated by the world's remaining gasoline/diesel vehicle fleet, with a total GHG contribution of 66-74%. A quick ramp-down of fossil fuel usage in transport applications is therefore a crucial factor to minimize cumulative GHG emissions. Sustainable drop-in fuels are one option to eliminate net GHG emissions of existing internal combustion engine (ICE)-powered vehicles. The use of first-generation (1G) biofuels like ethanol is common today, but when the volume ratio exceeds 10% in the fuel blend, flex-fuel engine technology is required. For compression ignition (CI) or diesel engines, Fatty Acid Methyl Esters (FAMEs, also known as biodiesel) are widely used as a partial replacement for fossil diesel. The use of FAME as a low-blend component in transport fuel (up to 7 % in Europe, compliant to EN590) does not require any changes in the distribution system or the engine, but modifications to the distribution as well as the engine infrastructure (e.g. seals, piping) are required for use of 10% FAME/diesel blends up to 100 % pure FAME fuel. So neither ethanol nor FAME can be considered as drop-in fuels. For CI engines, a second-generation alternative is available in the form of HVO (Hydrotreated Vegetable Oil). HVO claims to be a true drop-in fuel that can be used in legacy CI-powered vehicles. It is produced from waste, residues and dedicated crops not in competition with food crops and makes up for an estimated 7% of biofuels consumed in 2020, according to the International Energy Agency's Transport Biofuel report of that year. The production of sustainable drop-in fuels for legacy spark ignition (SI) engines is less established. Sustainable synthetic EN-228 compliant gasoline, made out of ethanol is already available today, though in very limited quantities [2]. Production capacity for green methanol-based synthetic gasoline is expected to increase considerably in the coming years [3]. Complementary to these production efforts, a novel biorefinery process designed by researchers at KU Leuven generates naphthenic biofuel components that might be used as drop-in fuels for SI engines. Although the production cost of naphthenic biofuels with the Ad-Libio process is currently unknown, an economic study is foreseen within the project and will be completed at the end of 2023. However, some major potential advantages of Ad-Libio over fermentation processes can already be identified. The process efficiency is situated between 70 to 80%, which is an improvement compared to the 50% that are associated with fermentation processes. Ad-Libio omits the use of woody biomass-compatible yeasts that are complex to synthetize, costly to produce and hard to recycle. Also, Ad-Libio does not suffer from carbon loss in the form of CO_2-emissions like fermentation processes do. Contrary to fermentation processes, Ad-Libio does not have alcohols as main output stream, but C5-C6 hydrocarbons that will likely not require flex-fuel technology for them to be used as combustion engine fuel.

The initial Ad-Libio production process

In the Ad-Libio process [4], debarked and milled wood particles undergo basic extraction of the non-structural compounds such as fats, oils, proteins and terpenes. Then, lignin (step 1, Figure 1) is extracted from the lignocellulosic network in the presence of an alcohol solvent and subsequently stabilized by catalytically depolymerizing it in stable fragments. Next to the lignin oil, cellulose pulp is retained, which predominantly consists of C6 and C5 sugars. This fibrous sugar pulp is then further treated with hydrogen molecules, resulting in a hydrocarbon mixture in the naphtha-range (C5-C6 molecules)

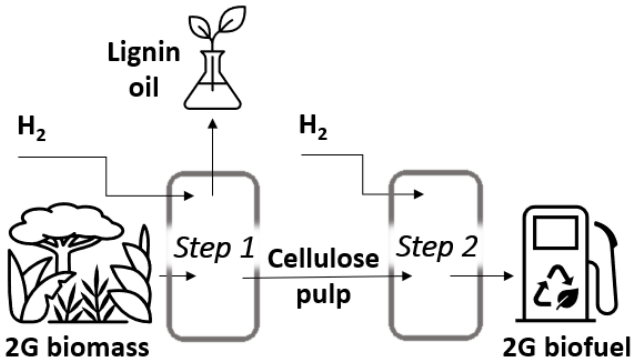

Figure 1. The Ad-Libio production process.

The initial composition of the process outcome was theoretically defined by the chemists at KU Leuven and were listed. The data mentioned in table 1 were extracted from a SI fuel database from RWTH Aachen university [7]. This database contains more than 600 fuel components and lists, for each component, the physical and chemical properties including research and motor octane numbers, octane sensitivity, cetane number, heat of vaporization, liquid density, surface tension, viscosity, boiling point, melting point, vapor pressure, lower heating value, H/C ratio, oxygen content, molecular weight, and water solubility. Most of the listed values are experimentally determined but in the case of missing experimental evidence, values are estimated by using an artificial neutral network-based octane number model or other established quantitative structure-property relationship models.

Table 1. Initial Ad-Libio fuel composition.

Ad-libio fuel component	**Vol %**	**RON**
n-hexane	70	24.8
n-pentane	13	61.7
Methyl cyclopentane	9	91.3
2-methylpentane	1	73.4
cyclopentane	1	101.3
3-methylpentane, methyl/ethyl/propyl- cyclohexane, et al.	5	45-103
tetrahydrofuan, (di)methyl tetrahydrofuran	1	73-101
Result of the fuel blend (linear molar calculation)		**41.2**

The listed components were investigated for usability as a drop-in replacement for gasoline, starting with the fuel's research octane number (RON). To predict the octane number of the blend, a fuel blend calculator from Bath University was modified, to enable blend calculations of up to 20 blend components. For simplicity, a linear molar relationship was used to calculate the RON of the blend, as shown in equation (1)

$$RON_{blend}=\Sigma x_i.RON_i \quad (1)$$

The result of the blend calculator, mentioned in table 1, was a RON of 41,2 for the blended components. The calculated result was experimentally verified by means of a CFR engine with variable compression ratio (CR), using a simplified approach. A fuel's octane rating was estimated by generating a fixed average peak pressure pulsation (APPP) value from 200 knocking cycles, expressed in kPa, by reading the corresponding CR. Comparing this CR with the one at which a primary reference fuel mixture (PRF) knocks with the same APPP then yields an estimation of the fuel's octane number [7]. Although this experimental method is not ASTM D2699-compliant [6], it was sufficient to confirm the previously made calculations. A measured octane number (ON) value of 37.9 compared to a calculated ON of 41.2 indicated a difference of slightly more than 10%, but this can be subscribed to the fact that at low octane numbers, the experimental method becomes less accurate.
Compared to a minimum RON of 95 according to the European norm EN228 for gasoline, it is clear that the initial process output of the Ad-Libio was not suitable as a drop-in replacement for gasoline.

Revised production process outcome

After feedback with KU Leuven, the production process parameters were altered in an attempt to increase the RON of the end product. By varying different process parameters, isomerization of the initial molecules could be obtained and different alternative process outcomes could be calculated. Table 2 lists ten different

theoretical fuel blends, with each "x" indicating the presence of a fuel component in the blend. For simplicity, the exact volume fractions of the components are not listed.

Table 2. Initial Ad-Libio fuel composition.

Blend #	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Pentane	x	x		x	x	x	x	x	x	x
Methylbutane		x	x	x	x	x	x	x	x	x
Hexane	x	x		x	x	x	x	x	x	x
2-methylpentane		x	x	x	x	x	x	x	x	x
3-metylpentane		x	x	x	x	x	x	x	x	x
2,2-dimethylbutane		x	x	x	x	x	x	x	x	x
2,3-dimethylbutane		x	x	x	x	x	x	x	x	x
Ethanol					x	x	x	x	x	x
Pentanol				x						
Hexanol				x						
Methylfuran						x				
Dimethylfuran						x				
Methylbenzene							x	x	x	x
Ethylbenzene							x	x	x	x
Propylbenzene							x	x	x	x
1- & 2-pentene								x		x
1-, 2- & 3-hexene									x	x
Calculated RON	**38**	**76**	**84**	**71**	**82**	**91**	**94**	**95**	**92**	**94**

The fuel blend calculator proved to be helpful by providing fast estimated RON calculations of every blend. It is clear that the isomerization of the original molecules leads to a significant increase in knock-resistive properties of the Ad-Libio fuel, with blend #8 being the most promising. It was decided to synthesize this specific blend in the lab and have it tested for research octane number (RON), motor octane number (MON) and Reid vapor pressure according to ASTM. The results confirmed the initial calculations with a RON of 96.2, a MON of 86.5 and a RvP at 37,8°C of 47.3 kPa.

Conclusions

A new 2G drop-in biofuel serving SI engine applications is under development. Thanks to a fuel blend property calculator, quick decisions could be made to tune the production process, turning its outcome into a promising fuel that may possibly be used as a drop-in replacement for gasoline. Further investigation with regards to performance and emissions with real-life engines is necessary and is planned for the forthcoming year.

References

[1] Research Association for Combustion Engines, "*FVV Future Fuels Study IV: Final report"* (2021)

[2] Esarte, C. "Development of 100% Renewable EN228 Gasoline Formulation and its Compatibility with Different Elastomeric Materials", *Proc 10th International Conference Fuel Science – From Production to Propulsion.* Aachen, Germany, 2022.

[3] Hannibal, W., *E-fuels and Hydrogen in Mobility Conserve the Earth's Resources*, MTZ worldwide, 2022. p. 66.

[4] Op de Beeck, B., et al., "Direct catalytic conversion of cellulose to liquid straight-chain alkanes", *Energy & Environmental Science*. 8(1): 230-240 (2004)

[5] vom Lehn, F., et al., "A property database of fuel compounds with emphasis on spark-ignition engine applications", *Applications in Energy and Combustion Science*. 5: p. 100018 (2021)

[6] ASTM D2699-15a., *Standard Test Method for Research Octane Number of Spark-Ignition Engine Fuel*, ASTM International, 2015

[7] Robeyn, T., Larsson, T., Verhelst, S., et al., "Development of a Novel Drop-in Naphthenic Spark Ignition Biofuel by Means of a Fuel Blend Calculator and a Simplified Octane Number Verification Method", *SAE Technical Paper* 2023-01-0317 (2023)