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PART 1

Second and Third Generation Biofuels: Towards Sustainability and Competitiveness

Deuxième et troisième génération de biocarburants : développement durable et compétitivité

Oil & Gas Science and Technology – Rev. IFP Energies nouvelles, Vol. 68 (2013), No. 4, pp. 621-783

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Rational Formulation of Alternative Fuels using QSPR Methods: Application to Jet Fuels

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Résumé — Développement d'un outil d'aide à la formulation des carburants alternatifs utilisant des méthodes QSPR (*Quantitative Structure Property Relationship*): application aux carburateurs —

Le développement des carburants alternatifs est en plein essor, notamment dans le domaine aéronautique. Cela se concrétise par la possibilité d'incorporer jusqu'à 50 % de carburants de synthèse de type Fischer-Tropsch (FT) ou *hydroprocessed esters and fatty acids* (HEFA) dans du carburateur. De même, ces carburants paraffiniques se développent pour le transport terrestre en parallèle des biocarburants à base d'esters ou d'alcool actuellement disponibles. La formulation de ces carburants alternatifs est actuellement basée sur une sélection des produits *via* des critères physiques. L'atteinte de ces critères se fait souvent par des formulations empiriques et ce type de fonctionnement ne s'avère pas très efficace et montre ses limites. En effet, les carburants alternatifs présentent des propriétés chimiques qui peuvent être différentes en fonction du procédé (répartition *n*-paraffines/iso-paraffines, longueur de chaîne, ramification, etc.) et donc modulable. Ainsi, une nouvelle voie pourrait être envisagée visant à déterminer par le calcul, la molécule (ou le mélange de molécules) la plus à même de répondre au cahier des charges du carburant, puis à étudier ou à optimiser les voies de synthèse permettant d'accéder à ces produits.

Le travail présenté a pour objectif le développement et l'application de méthodes QSPR (*Quantitative Structure Property Relationship*) permettant de relier la structure aux propriétés d'une molécule. Les produits étudiés sont les hydrocarbures (normal et iso-paraffines, naphènes, aromatiques, etc.) et les oxygénés du type alcools et esters. Les propriétés ciblées sont celles figurant dans les spécifications carburants telles que le point d'éclair, l'indice de cétane, la masse volumique et la viscosité. Les modèles prédictifs des propriétés des corps purs ont été établis à partir de données expérimentales de référence provenant en grande partie de la littérature. L'utilité de tels modèles dans la sélection de composés d'intérêt peut être montrée par exemple pour trouver le meilleur compromis pour satisfaire les critères de tenue à froid et de masse volumique des paraffines. Ainsi, si la chaîne carbonée est trop longue alors le critère de tenue à froid risque de ne pas être satisfait. Il est alors nécessaire de favoriser la ramification ou d'ajouter des bases ayant une bonne tenue à froid comme certains naphènes ou monoaromatiques alkylés. Cependant, cela entraîne bien souvent une masse volumique trop basse par rapport à la spécification. Là encore l'ajout de naphènes ou de monoaromatiques alkylés issus de la biomasse peut être intéressant.

Abstract — Rational Formulation of Alternative Fuels using QSPR (*Quantitative Structure Properties Relationship*) Methods: Application to Jet Fuels — Alternative fuels are a promising solution for road transport but also for aircraft. In the aviation field, a huge amount of work has been done in the past years with the approval to use up to 50% by volume of SPK (Synthetic Paraffinic Kerosene) in blends

with conventional fossil Jet A-1. SPK are Fischer-Tropsch (FT) fuels but also Hydroprocessed Esters and Fatty Acids (HEFA). However, these alternative fuels can have different chemical properties depending on the process used for their production. These properties include normal to iso paraffin ratio, carbon chain length and level of branching.

R&D studies of alternative fuels are based on the evaluation of products coming from identified production processes. However, it appears that a better way of studying them could be firstly to determine the best chemical composition regarding aviation problems and secondly to find the best process and finishing process in order to obtain such a product.

The objective of this work is to design a tool that aims to guide the future formulation of alternative fuels for aviation through the prediction of targeted physical properties. Thus, it is proposed to apply a methodology that identifies relationships between the structure and properties of a molecule (QSPR for Quantitative Structure Property Relationship), with the aim of establishing predictive models. These models will be built for hydrocarbons (normal and iso paraffins, naphthenes, aromatics, etc.) and oxygenated compounds (esters and alcohols). For aviation, oxygenated compounds are not considered as a drop-in fuel. It could be seen as a disruptive solution in a long term view. There are concerns with oxygenates in aviation that are covered in this paper such as the flash point but others such as the energetic content, the water affinity that are not taken into account in this paper. The properties currently studied are flash point, cetane number, density and viscosity. The data sets will contain data from the literature, from experimental measurements and from molecular simulations for complex molecules. The interest of such models in the selection of molecules can be shown for example by the trade-off between cold flow properties and density of paraffinic compounds. If the carbon chain length is too high, the cold flow properties are compromised. One solution can be to increase branching or incorporate fuel base with good cold flow properties such as naphthenic or aromatic compounds. However, this leads to a decrease in density below the jet fuel specification. Again, using naphthenic or alkyl-aromatic compounds produced from biomass can help.

ABBREVIATIONS

AAE	Average Absolute Error
AARE	Average of the Absolute Relative Errors
ASTM	ASTM International, formerly known as the American Society for Testing and Materials (ASTM)
CFR	Cooperative Fuel Research
CN	Cetane Number
DIPPR	Physical as Design Institute for Physical Properties
FBP	Final Boiling Point
FF-ANN	Feed-Forward Artificial Neural Networks
FGCD	Functional Group Count Descriptor
FP	Flash Point
FT	Fischer–Tropsch
GFA	Genetic Function Approximation
GM	Graph Machines
GRNM	General Regression Neural Networks
HEFA	Hydroprocessed Esters and Fatty Acids
HIS	Hydroisomerization
HVO	Hydrotreated Vegetable Oil
IBP	Initial Boiling Point
IPK	IsoParaffins Kerosene
MD	Molecular Descriptor
PLS	Partial Least Squares regression
QSPR	Quantitative Structure Properties Relationship

R^2	Coefficient of determination
RMSE	Root Mean Square Error
SPK	Synthetic Paraffinic Kerosene
SVM	Support Vector Machines

INTRODUCTION

Background and Properties of Interest

The development of alternative fuels is currently in progress. It is taking place in the automotive sector all over the world. In Europe, the deployment of biofuel for automotive applications is done step by step, by increasing the ratio of biofuel into conventional fuel and also by clarifying environmental criteria that take into account, for example, the competition with food or water consumption. The Renewable Energy Directive (RED) [1] goal is to reduce greenhouse gas (GHG) emissions through the use of energy originating from renewable sources, in particular in transport. A 20% target for the overall share of energy from renewable sources and a 10% target (in energy content) for energy from renewable sources is expected in transport by 2020. The RED directive established a first set of sustainability criteria for biofuels that relates mainly to the following environmental issues: biodiversity, protection of ecosystems and reduction of greenhouse gas emissions. It is not specified yet how the aviation sector will be dealt with the 10% target in transport. For automotive,

the biofuel ratio into conventional fuel is at present 10% volume for ethanol into gasoline and 7% volume for biodiesel into gasoil. The 10% target in energy content of the RED directive corresponds to a ratio of around 15% volume for ethanol into gasoline and 10% volume for biodiesel into gasoil. So an increase of biofuel ratio in conventional fuel is expected.

The aviation industry, as a part of the transport sector, contributes to CO₂ emissions with about 2% of the total anthropogenic CO₂ and 13% of the transport part [2]. While this contribution to CO₂ emissions is minor, air traffic is expected to grow in the coming years. Indeed air traffic is expected to grow annually by 3-5% for passengers and 9-10% a year for airfreight for the next 20 years [3]. This implies an increase in the fuel demand that will be offset by engine and air frame efficiency improvements. Thus, the aviation industry will have to face the challenge of reducing GHG emissions. The International Air Transport Association (IATA) committed to stop the growth of CO₂ emissions from 2020 (neutral growth) and to halve emissions by 2050 compared to 2005 levels (baseline). Actually, improvements in technology, Air Traffic Management (ATM) and operations will lead to a sizable emissions reduction. However, as seen in Figure 1 [4], the aviation industry's ambitious goals will

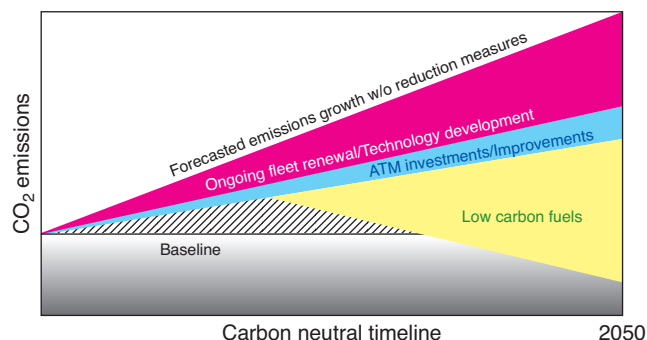


Figure 1

Key factors for CO₂ emissions reduction in aviation (extracted from the IATA report) [4].

only be met with a significant contribution from low carbon alternative fuels. Moreover, the use of alternative fuels can also be seen as a way to secure the supply. In addition, EU goal is to use 40% of sustainable low carbon jet fuels by 2050 [5].

The deployment of biofuel in aviation is already in progress. Since 2009, jet fuel ASTM specification has approved blends containing up to 50% volume of Fischer-Tropsch (FT) type fuels and this has been followed in 2011 by the possibility to add up to 50% volume of Hydro-processed Esters and Fatty Acids (HEFA) (ASTM D 7566 [6]). However, it is anticipated that more candidate blend stocks from other pathways will go through the approval process [7]. This specific approval process for aviation fuels (ASTM D4054 [7]) is complex and needs a large amount of fuel to be completed. It is why modelling properties could be of great importance to evaluate the potential of alternative fuel candidates before entering the long and expensive process of certification and could be seen as a first level of screening. The aim is to reduce the time and product consumption of fully experimental approaches by rationalizing the formulation of alternative fuels using Quantitative Structure Properties Relationship (QSPR) approaches.

Aviation represents a very specific and constraining mode of transportation, due to its usage (short, middle, long ranges with the same fuel, worldwide availability of the fuel, etc.) and its compulsory safety constraints. Properties of jet fuel can be divided into three main families: properties linked to combustion, properties linked to use at high altitude (large range of pressures and temperatures) and properties related to storage and safety.

As a consequence, this work is focused on the following stringent properties for aircraft but also for automotive fuels: Flash Point (FP), Cetane Number (CN), density and viscosity. Indeed this work has been initially dedicated to jet fuel but can be easily extended to the automotive sector. Table 1 provides the fuel specifications applied in Europe and USA for the stringent properties. FP is an issue for the aviation sector and it is one reason ethanol has been rejected as a jet fuel component and why ethanol-containing gasoline should not be allowed to contaminate jet fuel. It is also important to

TABLE 1

Examples of fuel specification applied in Europe (EN or DEF STAN) and USA (ASTM) for FP, CN, density and viscosity

	Gasoline		Diesel		Jet A-1	
	EN228	ASTM D 4814	EN590	ASTM D 975	DEF STAN 91-91	ASTM D 1655
FP (°C)	-	-	Min 55	Min 38	Min 38	Min 38
CN (-)	-	-	Min 51	Min 40	-	-
Density (kg/m ³)	720-775 at 15°C	-	820-845 at 15°C	-	775-840 at 15°C	775-840 at 15°C
Kinematic viscosity (mm ² /s)	-	-	2.0-4.5 at 40°C	1.3-2.4 at 40°C	Max 8.0 at -20°C	Max 8.0 at -20°C

point out that CN is not a jet fuel property. However, CN is a relevant property for jet fuels in Diesel aircraft engines (but the specification does not cover that minority use area) and Diesel engines in military applications. Another point to specify about the CN: there are Cetane Number and cetane index. Cetane Number is measured on CFR engines (see more detail in *Sect. 1.2* on properties) while cetane index is computed from density and distillation data. It is why Cetane Number is affected by cetane boosting additives and cetane index is not.

This work covers the field of conventional fuels and alternative fuels for aviation and automotive applications. It is why the products studied are hydrocarbons such as normal and iso-paraffins, naphthenic compounds, aromatics, olefins but also oxygenated compounds such as alcohols and esters. Alternative fuels are synthetic fuels originating from FT synthesis, Hydrotreated of Vegetable Oils (HVO), also called HEFA. HVO and FT products contain normal and iso-paraffins [8, 9]. Naphthenic and aromatic compounds can be obtained from the liquefaction or the pyrolysis of biomass [10, 11]. Oxygenated compounds such as alcohols can be produced by fermentation techniques and esters by transesterification of vegetable oils such as rapeseed, sunflower, palm or jatropha [12].

For each family, a different trade-off has to be found in their formulation. Paraffins can be described by their carbon chain length, their isomerisation ratio and their cyclisation rate. As already mentioned, normal paraffins with large chain length have a bad cold flow behaviour whereas branching is favourable but induces a decrease of the CN. For paraffinic fuels such as FT products and HVO, finding this trade-off is really important.

The introduction of oxygenated compounds for aeronautics fuels such as esters and alcohols is a solution out of the scope of conventional chemical compounds, it is why these components are consequently considered as “non drop-in” fuels for aeronautics. Esters are used currently in Diesel fuel. However a trade-off between the main carbon chain length and branching, unsaturation (the number of carbon-carbon double bonds) has to be found in order to obtain a convenient product regarding specifications (cold behaviour, oxidative stability) [13].

About QSPR Modelling

Large number of predictive models developed during the last few years for these properties are based on QSPR approaches [14]. QSPR deals with statistical methods. It relates properties of interest with the molecular structure described by a variety of Molecular Descriptors. Molecular Descriptors are various molecular-based theoretical parameters which can be calculated using known mathematical algorithms solely from molecular structures. Molecular Descriptors can be classified into several categories: one-dimensional (1D), two-dimensional

(2D) and three-dimensional (3D), depending on the level of information necessary to compute them. Several MD are selected as the QSPR inputs to simulate multivariable model for the desired property of compounds. The QSPR method possesses some obvious advantages. The descriptors used in the QSPR models may have definite physical meanings, which would be useful to probe the physicochemical information that shows a significant contribution to the targeted properties. Because only theoretical descriptors derived solely from the molecular structure would be involved and have continuous values, the QSPR models developed should theoretically be applicable to any organic compound belonging to the families of compound studied.

In QSPR studies, the selection of appropriate modelling techniques which can be applied to construct models is one of the key problems involved. At present, many different methods, such as Multiple Linear Regression (MLR), Partial Least Squares (PLS) and different types of Artificial Neural Networks (ANN) have been widely used in the QSPR modelling, which can be used for the inspection of linear and nonlinear relations between properties and MD. In this work, we propose a rigorous methodology based on the construction of consensus models.

The final target of this work is actually the development of models for fuel blends but the present work is only concerned with pure compounds. The objective is to guide the future formulation of alternative fuels with the help of the simulation of targeted physical properties. The paper is organized as follows: in Section 1, we detail the products, the properties, the databases, the method and the models used; Section 2 is dedicated to the presentation and discussion of the results on the prediction of the different properties, on the comparison between experimental and predicted values, on the predicted trends *versus* the carbon number; Section 3 is dedicated to the synthesis with focus on the possible trade-off between the properties. Finally, a conclusion ends the article highlighting the major results.

1 MATERIALS AND METHODS

1.1 Products

Table 2 gathers global characteristics of conventional fuels. The chemical family that composes conventional fuels are paraffin (normal and iso), naphthene, olefin and aromatic.

1.2 Properties Modelled

The development of models is done for the prediction of the following properties: Flash Point (FP), Cetane Number (CN), density and viscosity.

Safety-related properties are crucial for jet fuels and this is made apparent in the specification by a stringent limit on the FP. The FP defines the lowest temperature at which the

TABLE 2
Typical characteristics of conventional fuels

Product	Density at 15°C (kg/m ³)	Distillation (°C)		Carbon number	Composition (%vol)			
		IBP	FBP		Paraffin	Naphthene	Olefin	Aromatic
Gasoline	720-775	30-35	180-200	4-10	40-65	0-5	0-18	35
Jet	775-840	140-150	260-300	9-13	50-65	20-30	< 5	10-20
Diesel	820-845	160-180	340-370	10-20	50-65	20-30	0	10-30

vapour of a volatile liquid ignites when brought into contact with a flame. In the specific case of jet fuels, the specifications require the FP to be of at least 38°C [15].

The control of the combustion is also an important parameter. However, there are no specification requirements regarding ignition for jet fuels, whereas it is expressed by the CN in Diesel fuel. The CN mimics the tendency of a molecule to autoignite when exposed to heat and pressure, as it happens in a Diesel engine under working conditions. Two standard compounds are used to define the CN scale: isocetane (2,2,4,4,6,8,8-heptamethylnonane, also called HMN) and cetane (*n*-hexadecane), which are fixed to 15 and 100, respectively. CN, which is used to quantify the combustion quality in Diesel engines, is required by the ASTM D975 [16] to be at least 40 and by EN590 [17] to be at least 51. CN measurements are time-consuming and require a large volume of sample (about 1 L) when obtained by running the product in a single-cylinder Cooperative Fuel Research (CFR) engine according to ASTM D613 [18] or EN ISO 5165 [19].

Density is important because it directly relates volume to weight in the fuel tank and indirectly with the energy content, especially for traditional jet fuel but it may be less reliable for fuels with alternative components in them. ASTM specifications for jet fuels include a density between 775 and 840 kg/m³ at 15°C and for Synthetic Paraffinic Kerosene, SPK (FT and HEFA) include a density between 730 and 770 kg/m³ at 15°C.

Viscosity influences the lubrication properties as well as the combustion properties of the fuel. Low viscosities can lead to poor lubrication, which can cause excessive wear and leakage in the injection system. Higher viscosities can also induce pumpability issues, obstruction of the hoses or poor atomization of the fluid leading to poor combustion and an increase in pollutant emissions. The case of aircraft fuels is of particular importance since they are exposed to extreme temperatures. ASTM specifications for jet fuels include a maximum kinematic viscosity of 8 mm²/s at -20°C. Indeed this extreme temperatures occur essentially in the tank and there is a need that the fuel must be still pumpable and fluid. It is why a maximum limit has been established for viscosity at -20°C.

In the specifications, the methods recommended for the measurement of the different properties are indicated.

Sometimes several methods can be recommended for a single property. These methods can be different between gasoline, jet and Diesel fuels. However the precisions are evaluated to 0.5°C for FP, 5 for CN for a given range, 5.10⁻⁴ kg/m³ for density and 0.1 mm².s⁻¹ for viscosity. It can be underlined that the measurement of the CN is not very accurate. Moreover, as many jet fuels would not have CN within the method, the precision will be important.

1.3 Methodology

The methodology used to develop models concerning the prediction of the targeted properties is fully documented in previous papers [20, 21]. The main steps are described in Figure 2.

The 1st step consists in building the local database from external databases. Indeed the database is of major importance as the predictive quality of QSPR models is largely influenced by its size and its quality. The database was built on the basis of experimental data gathered from different sources, such as the Design Institute for Physical Properties (DIPPR), database of chemical companies, the chemical database of the University of Akron (Ohio, USA) and the information available in Yaws' handbook [22-27]. It is important to notice the peculiarity of the CN database which was built on the basis of the compendium by Murphy *et al.* [28] for oxygenated compounds and from Creton *et al.* [29] for hydrocarbons. The local and complete database contains FP of 625 molecules, CN of 299 molecules, 5 634 experimental density values for 730 molecules and 3 547 experimental viscosity for 407 molecules. Density and viscosity are properties that depend on temperature.

Before building the QSPR models, the main database was split into three subsets:

- the training set, used to train each learning algorithm;
- the validation set serves as an additional tool to estimate the predictive error of individual QSPR models, as well as an indicator to determine which models generalize better;
- the test set, used to estimate the predictive error of the final model.

The split was carried out using a random sampling function. The data subsets for training, validation and test sets consist of 70, 20 and 10% of the entire database, respectively.

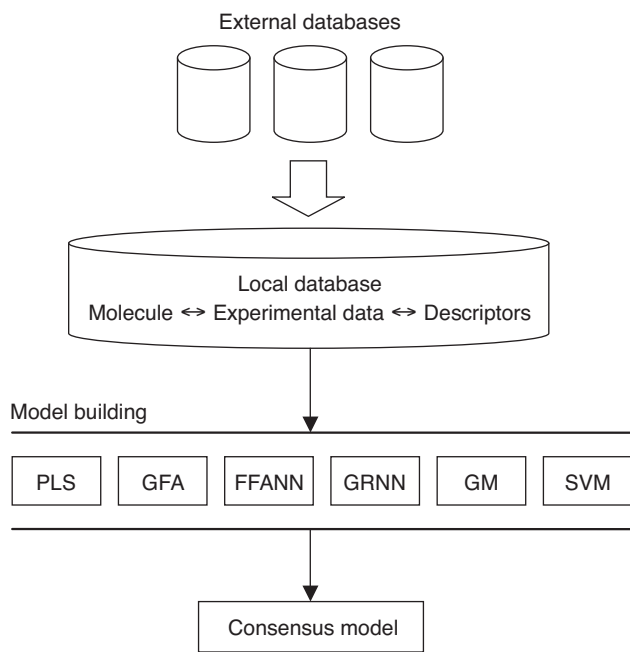


Figure 2

Outline of the methodology for the development of a consensus model.

The local database is then completed by the definition of descriptors for each molecule. Two sets of descriptors were used: Molecular Descriptors (MD) and Functional Group Count Descriptors (FGCD).

The next step is dedicated to the building of models. The analysis of the data was managed by the use of two kinds of models: linear models and nonlinear models. Linear models were obtained using approaches such as Genetic Function Approximation (GFA) and Partial Least Squares regression (PLS). Nonlinear models were obtained using approaches such as Feed-Forward Artificial Neural Networks (FF-ANN), General Regression Neural Networks (GRNN), Graph Machines (GM) and Support Vector Machines (SVM).

The final step is the work on the consensus model and is an innovative approach to improve predictions. Indeed, in our previous work we have seen that, when averaging the predictions of different models, the robustness of the resulting consensus model is better than that of the individual models used to build it [20, 21]. This is why, in this work, this methodology has been applied and all possible models (*i.e.*, weighted combinations of individual model predictions) were ranked based on their performance on the validation set. For each property, a final performance test of the generalization ability was carried out by looking at the performance of the best consensus model performed on the test set. Full details about the methodology and validation of models are given in our previous works [20, 21].

2 RESULTS

2.1 Flash Point

The consensus model is used to predict FP of a range of compounds. FP trends with the number of carbon atoms are presented in Figure 3 for hydrocarbons.

In Figure 3, the FP increases when the number of carbon atoms in the molecule increases whatever the chemical structure (normal paraffins, iso-paraffins, cyclo-paraffins and aromatics). The 1st order parameter for the FP is the total carbon number as it is underlined by the iso-carbon atom number curves in the figure. For example, the FP is similar between decane and propylbenzene with respectively 320 K (47°C) and 323 K (50°C). Moreover moving a group (methyl or ethyl) from position 2 to positions 3, 4 and more on the main chain has scarcely any impact on the FP value. The specification limit for jet fuel is above 311.15 K which corresponds to molecules with 10 carbon atoms or more. For Diesel fuel, the limit is above 328.15 K which corresponds to a molecule having more than 11 carbon atoms. As indicated in Table 2, the carbon number for jet fuel is between 9 to 13 and between 10 to 20 for Diesel fuel. For FT-SPK components, as presented in Figure 4, the carbon number of the molecules is between 8 to 16. In fact, we must be careful as fuels are blends and not pure compounds. So we cannot directly transfer results from pure compounds to fuels.

The tendencies for alcohols are presented in Figure 5. FP of linear alcohols are higher than those of *n*-paraffins. Moreover, the FP of alcohols increases, at fixed number of

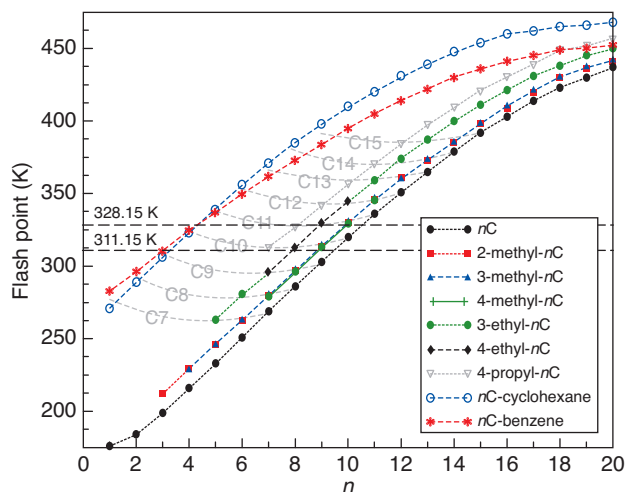


Figure 3

Tendencies of the FP evolution for some hydrocarbons when increasing *n*, the number of carbon atoms along the principal chain in some hydrocarbons. The iso-number of carbon atom curves are represented in dashed gray (extracted from the work of Saldana *et al.*) [20].

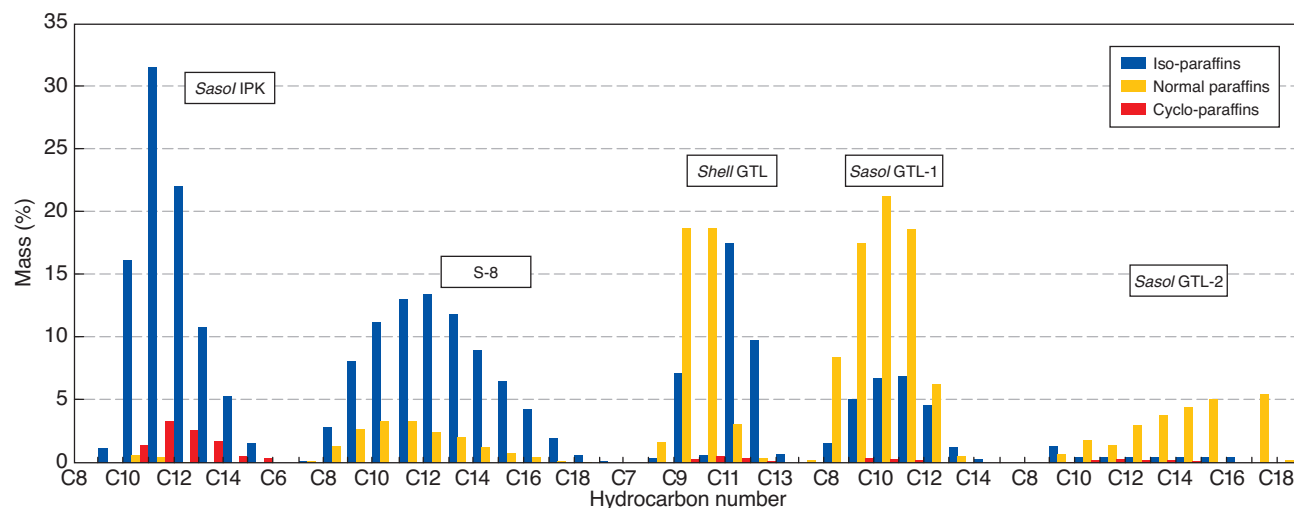


Figure 4

Distribution of hydrocarbons in five SPK fuels using GC*GC [30].

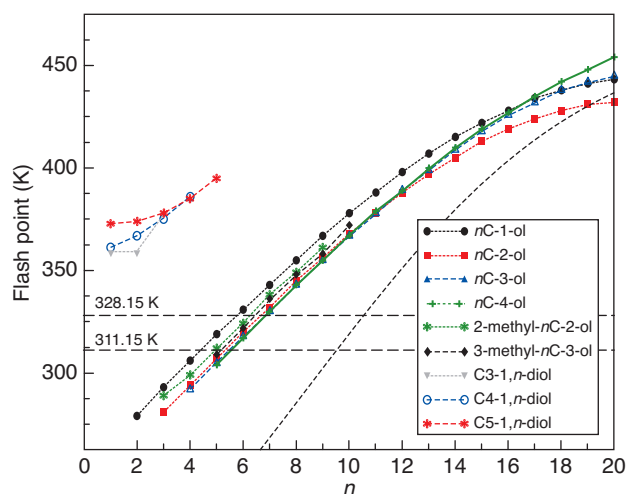


Figure 5

Tendencies of the FP evolution for some alcohols with the parameter n . The parameter n denotes either the number of carbon atoms along the principal chain or the position of a specific functional group. The dotted line presents FP values for n -paraffins (extracted from the work of Saldana *et al.*) [20].

carbon atoms, from primary alcohol to secondary alcohol and tertiary alcohol. Furthermore, molecules handling two alcohol functions are well above the limit of 311.15 K (38°C). The addition of alcohol to the fuel affects the FP. It is the case when ethanol is added to Diesel fuel [31] and jet fuel [32]. Ethanol is a small chain length alcohol with a low FP, predicted at 15.85°C and its addition to Diesel or jet fuel decreases the FP of blends. However ethanol is the most well-known alcohol, mainly used as alternative fuel for

spark-ignition engines. FP is one of the reasons why ethanol has been rejected as a jet fuel component and why ethanol containing gasoline should not be allowed to contaminate jet fuel. The issue with FP can be overcome by the use of higher alcohols. As can be seen in Figure 5, the specification limit is reached from and above pentanol for jet fuel (38°C) and from and above hexanol for Diesel fuel (55°C). However the use of higher alcohols could have a potential, provided that some production pathways are found. The prediction of the FP of blends is not obvious and could not be solved with a linear correlation [33].

2.2 Cetane Number

Figure 6 presents the CN evolution *versus* carbon number. It appears that the CN increases when the carbon number in the molecule increases, whatever the chemical structure except for diols. For n -paraffins, the specification limit is passed for octane and molecules with more than 8 carbon atoms. For cyclo-paraffins, represented by nC -cyclohexane, the specification is passed for pentylcyclohexane (total carbon number of 11). For aromatics, CN above 51 is obtained first for decylbenzene (total carbon number of 16). This reflects the well-known tendencies which are:

- CN of paraffins increases when the principal chain length increases but decreases with the number and the complexity of branching;
- double carbon bonds tend to decrease CN compared to the corresponding paraffin;
- bad ignition performance for alkyl-aromatics can be overcome by increasing the number of carbons in the lateral chain.

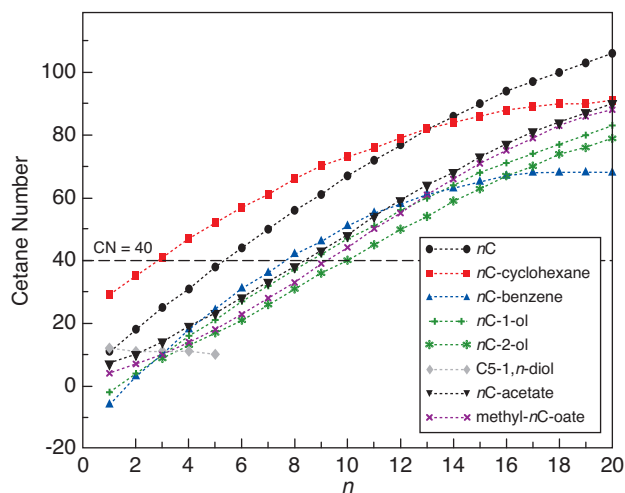


Figure 6

Tendencies of the Cetane Number evolution for some families of compounds with the parameter n , where n denotes either the number of carbon atoms along the principal chain or the position of specific functional group (extracted from the work of Saldana *et al.*) [20].

In the case of US Diesel fuel, hydrocarbons (n -alkanes or n -C) satisfying a CN of at least 40, which is the minimum limit required by ASTM D 975, are those containing a total number of carbon atoms of 6 and more.

Figure 6 also shows the impact of the presence of an alcohol group in a linear paraffin. Thus, the CN of n C-1-ol compounds are about 20 CN units lower than that of the corresponding n -paraffin. A 5 CN unit difference is observed between CN when the OH group is moved from position 1 to 2. It is interesting to notice that the predicted CN of ethanol is 4. The limit of a minimum of 51 for EN590 is passed for 11C-1-ol and 12C-2-ol.

The tendencies are also represented for n C-acetate and methyl- n C-oate. Esters generally used in Diesel fuel are similar

to methyl- n C-oate and are always a blend between different molecules of ester. They often contain double bonds. Table 3 shows the chemical composition and the CN of some usual esters added in Diesel fuel. The rules established above are respected between Rapeseed Methyl Ester (RME), Sunflower Methyl Ester (SuME), Soya Methyl Ester (SoME) and Palm Methyl Ester (PME). If the base considered is RME, the ratio of double carbon bond is increased for SuME and the result is a decrease of CN. It is also the case of SoME with a more important decrease of the CN compared to RME due to molecule with 3 double carbon bonds. PME has a greater CN than RME due to the increase of the ratio of molecule with 16 carbon atoms and no double bond. The calculated CN in the last column of Table 3 is obtained by using a linear regression between the mass ratio and the CN of pure molecules. This simple method gives results similar to the measured CN. The measurement of CN is by definition a linear method, in the absence of cetane improving additives and this explains the good agreement between computed and measured CN.

One may note that the consensus model gives calculated cetane values of 94, < 0 and 10 for respectively cetane, 1-methylnaphthlene and 2,2,4,4,6,8,8-heptamethylnonane. These molecules are used to define the CN scale as it is explained in the previous paragraph on properties. This predicted values are in agreement with the definition.

2.3 Density

Figure 7 presents the predicted trends for density at 15°C versus number of carbons for various chemical families (n -alkanes, iso-alkanes, alkyl-cyclohexanes, alkyl-benzenes, alcohols and esters).

Different trends are observed for families: paraffins (normal and iso)/cycloparaffins and alcohols/esters and benzenes. Indeed, short saturated esters appear to have the highest densities. According to the model, linear alkanes are generally more dense than iso-alkanes with the same total carbon number and the same is observed for linear and iso-alcohols. This is consistent with the idea that branching decreases the ability

TABLE 3

Chemical composition (wt%) and CN of some usual methyl esters added in conventional Diesel fuel [34, 35] (writing convention: C x :y means methyl ester with x carbon atoms and y the number of double carbon bond of the fatty part)

	C14:0	C16:0	C18:0	C18:0	C18:0	C18:0	Measured CN	Calculated CN
Rapeseed Methyl Ester (RME)		5	2.5	59	21	9	50	51
Sunflower Methyl Ester (SuME)		6	5	18	69	<0.5	49	49
Soya Methyl Ester (SoME)		10	4	23	53	8	48.1	50
Palm Methyl Ester (PME)	1	44	6	38	10	<0.5	64	65
Predicted CN	66	75	83	57	44	31	-	-

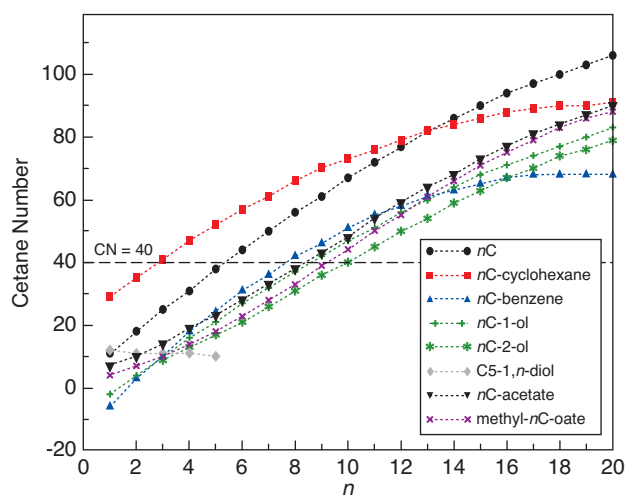


Figure 7

Tendencies of the density evolution for some families of compounds with the parameter n . The parameter n denotes the number of carbon atoms along the chain (extracted from the work of Saldana *et al.*) [21].

of molecules to pack well together. The resulting curves show that the density increases with the increasing number of carbon atoms for paraffins, cyclohexanes and alcohols. In the case of esters and to a lesser extent for alkylbenzenes the opposite is observed, *e.g.* density increases with decreasing chain length [36-39]. Furthermore, experimental and predicted values in the database indicate that unsaturated esters have higher densities than saturated esters, at a fixed number of carbon atoms. This trend has been attributed to the decreasing of the packing and thus the increasing of the free volume, which was also suggested by Shobha and Kishore [36] This behaviour was later explored through Monte-Carlo simulations performed using force field potentials developed by Ferrando [40] and was attributed to a change in the arrangement of the ester molecules.

The density limits for conventional jet fuel and alternative biojet fuel (SPK) are 775 to 840 kg/m³ and 730 to 770 kg/m³, respectively. The density has to be between 820 and 845 kg/m³ for conventional EU Diesel fuel and between 860 and 900 kg/m³ for ester added in Diesel fuel. These examples show that there can be a gap between the density limit of the final blend and the density limit of the alternative fuel added. Indeed it is important to take into account the chemistry of alternative fuels in order to have consistency between specifications. SPK are composed of paraffins and, as illustrated by Figure 7, paraffins are the least dense of all molecular sub-families. This explains why density specification for SPK fuel is lower than the conventional jet fuel. Esters are high density molecules and the density specification on esters is higher compared to Diesel fuel.

Density predictions of biodiesels based on their composition have been done using our consensus model predictions with Kay's mixing [21]. The Kay's mixing is a linear regression between molar fraction and the density of pure compound. The resulting deviations from the experimental biodiesel densities are all below 0.5%.

2.4 Kinematic Viscosity

The tendencies of kinematic viscosity, at 20°C and at 40°C, for some families of compounds *versus* number of carbon atoms are respectively presented in Figures 8 and 9.

The predicted trends show a marked difference between alcohols and all other families of compounds, with alcohols having much higher viscosity values than all other families of compounds. The same trends are observed at -20°C and at 40°C for kinematic viscosity, albeit with generally lower kinematic viscosity when increasing temperature. However, the difference between alcohols and the other families is less pronounced at the higher temperature.

Table 4 gives the predicted viscosities at -20°C and 40°C for molecules with a total of 13 carbon atoms. Some tendencies can be underlined. Indeed paraffins viscosity decreases with the number and the complexity of branching and also with aromatics.

TABLE 4
Predicted kinematic viscosities (mm².s⁻¹) at -20°C and 40°C
for molecules with a total of 13 carbon atoms

	At -20°C	At 40°C
<i>n</i> -alkanes	6.7	1.7
2-methylalkanes	4.9	1.4
4-propylalkanes	2.4	0.9
<i>n</i> -alkylcyclohexanes	1.5	0.7
<i>n</i> -alkylbenzenes	1.1	0.5

The specification limit for the kinematic viscosity at -20°C of jet fuel is below 8 mm².s⁻¹. This is the case for *n*-alkanes having a carbon number below 14. For Diesel fuel, the viscosity at 40°C has to be between 2 and 4.5 mm².s⁻¹ in the EU and between 1.3 and 2.4 in the USA. This is the case respectively for *n*-alkanes having a carbon number between 14 and 18 and between 12 and 14.

The prediction of viscosities of biodiesels based on their composition has been done from our consensus model with the Grunberg-Nissan mixing rule [21]. The Grunberg-Nissan mixing rule is a linear regression that links the logarithm of the viscosity of the blend with the logarithm of the viscosity of the molecule associated with their molar fraction. The absolute average relative error is 4.9%.

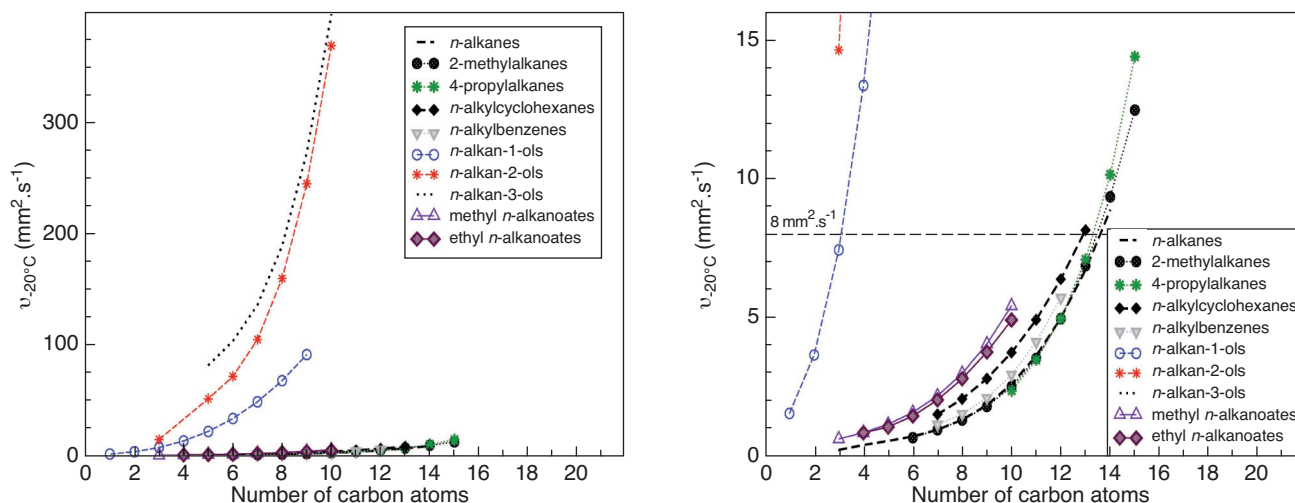


Figure 8

Tendencies of the -20°C kinematic viscosity evolution for some families of compounds with the parameter n . The parameter n denotes the number of carbon atoms along the chain (the right hand graph is a subsection of the left hand one – extracted from the work of Saldana *et al.*) [21].

3 TOWARDS APPLICATION

The predictive models previously described in this article are dedicated to pure compounds. It is a first approach and the work towards blends is currently in progress. The predictions of the properties of a blend of molecules could be done by linear interpolation for additive properties like CN, density and kinematic viscosity or by a more complicated methodology for properties like FP. The objective is to develop a tool for helping in blend formulation. For example, HVO and BtL (Biomass to Liquid) processes have a final step of up grading where the ratio of normal/iso/cyclo paraffins and the cut points, meaning the mean carbon number, is adjusted. This step has a direct impact on the yield of the different cuts (Fig. 10). Indeed, Figure 10 shows the evolution of the product distribution *versus* the cold flow properties targeted during the last process step of the hydrotreating of vegetable oil. The valuable products are Diesel and jet fuel. The jet and Diesel cut yields both decrease when the cold flow properties increase. In a 1st step, jet fuel yield increases but Diesel yield decreases and in a 2nd step, jet fuel yield and Diesel fuel yield decrease with the improvement of the cold flow properties. This competition for biofuel components affects the design and economics of facilities that convert bio-oils into fuel. Specifically, there is competition between gasoil (*e.g.* automotive Diesel, heating and industrial Diesel) and kerosene users. Most bio-oils naturally yield product in the gasoil range so further processing steps are needed to make a product that is technically better suited to kerosene (jet fuel) production, in particular having better low temperature features than those required for Diesel applications.

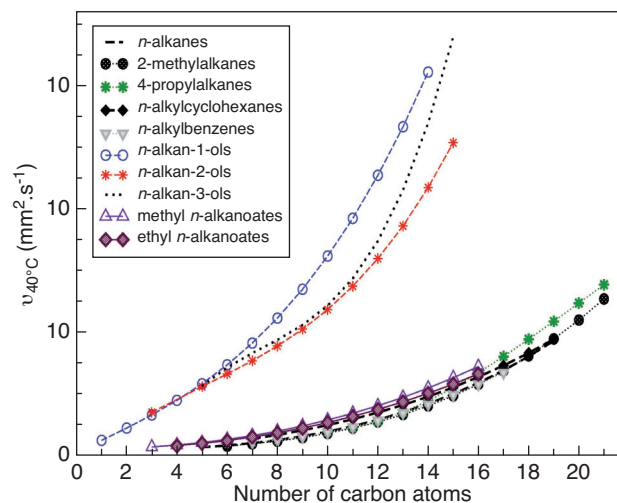


Figure 9

Tendencies of the kinematic viscosity evolution at 40°C for some families of compounds with the parameter n . The parameter n denotes the number of carbon atoms along the chain (extracted from the work of Saldana *et al.*) [21].

To illustrate the variability of alternative fuels, we can consider the chemical composition of biofuel for aircraft such as synthetic paraffinic kerosene (Fig. 4). It appears that there are varied compositions in terms of *n*/iso/cyclo paraffins ratio, of mean carbon atom number. The extreme products are *Sasol* IsoParaffinic Kerosene (IPK) that is composed mainly of iso-paraffins around C11 and *Sasol* GtL-1 that is composed of mainly *n*-paraffins around C10.

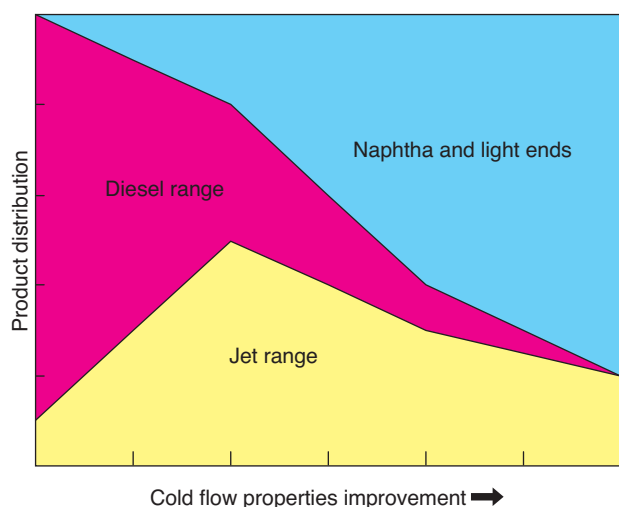


Figure 10
Impact of cold flow properties on kerosene yield of HVO [41].

CONCLUSION AND PERSPECTIVES

This work has shown that the prediction of several properties (Flash Point, Cetane Number, Kinematic viscosity and Density) is possible by a rigorous methodology through QSPR approach. The models have been shown to perform better than previously existing models on the range of chemical compounds (hydrocarbons, alcohols and esters) in which our study focuses (see previous papers [20, 21]). It is important to notice that the accuracy of the model depends on the accuracy of the experimental data.

A part of the work was dedicated to predict several trends that may help researchers and engineers to better visualize the behaviour of some compounds. This highlighted the fact that FP appears as mainly dependent upon the total number of carbon atoms in the molecule. The CN increases when the carbon number increases. For a same carbon number, the branching and the formation of cyclic molecules imply a decrease of CN. The density increases when the carbon number increases except for esters and to a lesser extent for alkylbenzenes. Linear alkanes are generally more denser than isoalkanes. This is consistent with the idea that branching decreases the ability of molecules to pack well together. It is also important to notice the high viscosity of alcohols and to a lesser extent of esters. The models take into account the impact of the temperature for the density and for the viscosity.

A simple and first approach allows to estimate the properties of some blends. It appears that, using a linear interpolation based on molar or mass fraction, it can be possible to evaluate properties such as CN, density and viscosity of some blends. However, the prediction of non-additive properties like FP will be more complex.

Moreover, it is important to develop this kind of approach to blends, as fuel formulation does not deal with pure compounds. It could also be interesting to integrate another parameter such as the process yield in order to deal with a global approach.

REFERENCES

- 1 Directive (2009) On the promotion of the use of energy from renewable sources, No. 2009/28/EC, April 23.
- 2 Pachauri R.K., Reisinger A. (2007) *Contribution of working groups I, II and III to the fourth assessment report of the intergovernmental panel on climate change*, Intergovernmental Panel on Climate Change (IPCC), Geneva Switzerland.
- 3 Advisory Council on Aeronautics Research in Europe (ACARE), (2010) *Aeronautics and air transport: beyond vision 2020 (towards 2050)*.
- 4 Steele P. (2009) on behalf of ACI, CANSO, IATA, ICCAIA, *Industry goals and measures to address CO₂ emissions from aviation, ICAO GIACC/3*, Montreal, Canada, 16-19 February.
- 5 EC (2011) *White Paper Roadmap to a single European transport area – Towards a competitive and resource efficient transport system*, 28 March.
- 6 American Society for Testing and Materials (2011) *Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons*, ASTM D7566 – 11.
- 7 American Society for Testing and Materials (2003) *Standard Specification for Qualification and Approval of New Aviation Turbine Fuels and Fuel Additives*, ASTM D4054 – 93.
- 8 Schulz H. (1999) Short history and present trends of Fischer-Tropsch synthesis, *Appl. Catal. A: Gen.* **186**, 3-12.
- 9 Murata K., Liu Y., Inaba M., Takahara I. (2010) Production of synthetic Diesel by hydrotreatment of Jatropha oils using Pt-Re/H-ZSM-5 catalyst, *Energy Fuels* **24**, 2404-2409.
- 10 Weiss W., Dulot H., Quignard A., Charon N., Courtiade M. (2010) Direct coal to liquids (DCL): High quality jet fuels, *27th Annual International Pittsburgh Coal Conference*, Istanbul, Turkey, 11-14 October.
- 11 Carlson T.R., Tompsett G.A., Conner W.C., Huber G.W. (2009) Aromatic Production from Catalytic Fast Pyrolysis of Biomass-Derived Feedstocks, *Topics Catal.* **52**, 241-252.
- 12 Mittelbach M., Remschmidt C. (2004) *Biodiesel The comprehensive handbook*, Boersdruck Ges.m.b.H, Vienna, Austria.
- 13 European Standards Organization (2010) *Standard Specification on the Quality of BioDiesel*, EN14214, CEN, Brussels Belgium.
- 14 Katritzky A., Kuanar M., Slavov S., Hall C.D. (2010) Quantitative correlation of physical and chemical properties with chemical structure: Utility for prediction, *Chem. Rev.* **110**, 5714-5789.
- 15 American Society for Testing and Materials (2007) *Standard Specification for Aviation Turbine Fuels*, ASTM D1655 – 07.
- 16 American Society for Testing and Materials (2011) *Standard Specification for Diesel Fuel Oils*, ASTM D975.
- 17 European Standards Organization (2009) *Standard Specification on the Quality of European Diesel Fuel*, EN590, CEN, Brussels Belgium.
- 18 American Society for Testing and Materials (2010) *Standard Test Method for Cetane Number of Diesel Fuel Oil*, ASTM D613.
- 19 European Standards Organization (2009) *Standard Test Method for Cetane Number of Diesel Fuel Oil*, EN ISO 5165, CEN, Brussels Belgium.

- 20 Saldana D.A., Starck L., Mougin P., Rousseau B., Pidol L., Jeuland N., Creton B. (2011) Flash point and cetane number predictions for fuel compounds using Quantitative Structure Property Relationship (QSPR) methods, *Energy Fuels* **25**, 3900-3908.
- 21 Saldana D.A., Starck L., Mougin P., Rousseau B., Ferrando N., Creton B. (2012) Prediction of Density and Viscosity of Biofuel Compounds Using Machine Learning Methods, *Energy Fuels* **26**, 4, 2416-2426. DOI: 10.1021/ef3001339.
- 22 Rowley R.L., Wilding W.V., Oscarson J.L., Yang Y., Zundel N.A., Daubert T.E., Danner R.P. (2003) *Design Institute for Physical Properties (DIPPR) Data Compilation of Pure Compound Properties*, American Institute of Chemical Engineers (AIChE), New York.
- 23 <http://www.sigmaaldrich.com>
- 24 <http://www.alfa.com>
- 25 <http://www.lookchem.com>
- 26 <http://ull.chemistry.uakron.edu>
- 27 Yaws C.L. (1999) *Chemical Properties Handbook: Physical, Thermodynamic, Environmental, Transport, Safety and Health Related Properties for Organic and Inorganic Chemicals*, McGraw-Hill, New York.
- 28 Murphy M.J., Taylor J.D., McCormick R.L. (2004) Compendium of Experimental Cetane Number Data, National Renewable Energy Laboratory (NREL), Golden, CO, SR-540-36805.
- 29 Creton B., Dartiguelongue C., de Bruin T., Toulhoat H. (2010) Prediction of the cetane number of diesel compounds using the Quantitative Structure Property Relationship, *Energy Fuels* **24**, 5396-5403.
- 30 Moses C.A. (2008) Comparative evaluation of semi-synthetic jet fuels, CRC project No. AV-02-04a, September.
- 31 Pidol L., Lecoite L., Jeuland N. (2009) Ethanol as a diesel base fuel: Managing the flash point issue – Consequences on engine behavior, *SAE Technical paper* 2009-01-1807.
- 32 Starck L., Sicard M., Ser F. (2009) Potential of alternative fuels for aircraft: Focus on thermal and oxidation stability, *11th International conference on stability, handling and use of liquid fuels*, Prague Czech republic, 18-22 October.
- 33 Liaw H.-J., Lu W.-H., Gerbaud V., Chen C.-C. (2007) Flash-point prediction for binary partially miscible mixtures of flammable solvents, *J. Hazardous Mater.* **153**, 1165-1175.
- 34 Ballerini D. (2011) *Les Biocarburants – Répondre aux défis énergétiques et environnementaux des transports*, Editions Technip, Paris France.
- 35 Cheah S.L. (2004) Analysis of engine performance using palm oil methyl ester, Dissertation towards the degree of Bachelor of Engineering, University of Southern Queensland.
- 36 Shobha H., Kishore K.J. (1992) Structural dependence of density in high molecular weight esters, *Chem. Eng. Data* **37**, 371-376.
- 37 Fandiño O., Pensado A., Lugo L., López E., Fernández J.J. (2005) Volumetric behaviour of the environmentally compatible lubricants pentaerythritol tetraheptanoate and pentaerythritol tetraoctoate at high pressures, *Green Chemistry* **7**, 775-783.
- 38 Gardas R., Johnson I., Vaz D., Fonseca I., Ferreira A.J. (2007) PVT property measurements for some aliphatic esters from (298 to 393) K and up to 35 MPa, *J. Chem. Eng. Data* **52** 737-751.
- 39 Pratas M.J., Freitas S., Oliveira M.B., Monteiro S.C., Lima A.S., Coutinho J.A.P. (2010) Densities and viscosities of fatty acid methyl and ethyl esters, *J. Chem. Eng. Data* **55**, 3983-3990.
- 40 Ferrando N. (2011) Potentiels intermoléculaires et algorithmes de Monte Carlo : application à l'étude des composés oxygénés, *Thèse*, Université Paris-Sud.
- 41 Starck L., Pidol L., Jeuland N., Chapus T., Bogers P., Bauldreay J. (2011) New route for increasing the aviation alternative fuels production and optimizing the biomass usage: Focus on HRJ, *12th International Conference on Stability, Handling and Use of Liquid Fuels*, Sarasota Florida USA, October.

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