

# Prediction of the PIONA and oxygenate composition of unconventional fuels with the Pseudo-Component Property Estimation (PCPE) method. Application to an Automotive Shredder Residues-derived gasoline.

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## Abstract

To check if an unconventional fuel can be burned in an engine, monitoring the stability in terms of composition is mandatory. When the composition of a conventional fuel cannot be measured for practical reason, it can be approximated using the API (American Petroleum Institute) relations (Riazi-Daubert) linking the hydrocarbon group fractions with well-chosen properties. These relations cover only the paraffin (coupling iso and normal), naphthene and aromatic (PNA) groups as they were developed for conventional fuels presenting neglected amounts of olefins and oxygenates. Olefins and oxygenates can be present in unconventional fuels. This paper presents a methodology applicable to any unconventional fuel to build a model to estimate the n-paraffin, iso-paraffin, olefin, naphthene, aromatic and oxygenate (PIONAO<sub>x</sub>) composition. The current model was demonstrated for an automotive shredder residues (ASR)-derived gasoline-like fuel (GLF). The model was trained using real fractions measured with a comprehensive two-dimensional gas chromatography coupled with flame ionization detector (GC × GC-FID) technique. The lowest cumulated absolute error comparing with the confidence interval of the measured fractions was evaluated to be 12.4%. The model was tested for one fuel composition only, therefore, the error of the calculated fractions will be investigated with other fuels in future work.

## Introduction

The number of end-of-life vehicles (ELV) is increasing over the years with a rate estimated at 2.25 %/y [1]. After the shredding process, approximately 75% of the matter is recovered as ferrous and 5% as non-ferrous metals [1,2]. The left fraction is called Automotive Shredder Residues (ASR) and can reach up to 25% of the ELV with only 15% recovered with the more advanced processes [2]. To limit the environmental impact of ASR that counted for more than 30Mt in 2013, Europe enforced new policies in the European Directive 2000/53/EC [3]. The reprocessing of wastes into new products and the use of wastes to replace raw matters are enhanced by the mean of objectives for the ELV recycling mass rate (85%) and for the ELV recovery mass rates (95%) respectively. Today, according to the end-of-life vehicle statistics published by the European Commission, the mean recycling mass rate in Europe reaches 85.7% but the mean recovery mass rate reaches only 91.3% [4].

Moreover, in the near future the Council of the European Union will probably increase the recycling rate objective. The Belgian company Comet Traitements and their partners came to a chemical process to convert the ASR, mainly composed of organic matter, into a crude oil-like fuel [1]. After its distillation, the synthetic fuel yielded a heavy fuel, i.e. a diesel-like fuel (DLF), and a light fuel, i.e. a gasoline-like fuel (GLF). The current work focuses on the GLF fraction.

The peculiar way the fuel was produced introduces an unusual composition. Conversely to conventional fossil fuels, the double bonds of the olefins in the ASR-derived fuels did not benefit of a long decomposition of matter to react and become saturated [5]. As a consequence, unconventional fuels may show a high number of olefins. Those fuels are also derived from plastics and are composed of a high amount of oxygenate molecules coming from the polymers themselves, like polyurethane (PUR) and polyamide (PA) [6]. The fuel treatment process, where the nucleofugic heteroatoms composing the raw matter as chlorine in polyvinyl chloride (PVC) are substituted by a nucleophile hydroxyl group, is also responsible for unusual composition. Further, plastics used in the automotive industry are composed of monomers with cyclic shapes as in the polystyrene (PS) polymer, increasing the aromatic content [6]. The peculiar properties of the fuel must be studied because they are driven by the content of the raw materials, by the cracking conditions and by the distillation parameters which depend on technical and financial constraints [7].

The unknown nature of the fuel creates a high failure risk for the cooperative fuel research (CFR) engine in which the fuel is tested to characterize the research octane number (RON) according to the standard test method ASTM D2699 [8]. This risk is mainly due to the presence of heteroatoms that could lead to a premature failure (saturation of the filters, obstruction of the fuel line due to deposits, corrosion by sulphur, abrasive wear due to metals or silicon oxides resulting of the combustion). If a property cannot be measured, it can be approximated thanks to the pseudo-component method, relying on the hydrocarbon group fractions and on the property of a representative molecule of each group to calculate a weighted average property [5]. However, unconventional fuels can have an unknown and complex chemical composition which makes it impossible to identify the whole chemical group repartition with a one-dimensional gas chromatography (GC) analysis. More advanced experimental techniques such as comprehensive two-dimensional gas chromatography (GC × GC) are time consuming and not always easily available.

Being able to approximate the fuel composition from easy to quantify properties that are measured anyway for technical needs (like the viscosity) enables two targets to be hit with one single set of tests. Methods exist to estimate the fuel composition if it cannot be measured experimentally but those have many limits. Riazi summarized the API (American Petroleum Institute) methods [5] based on the weighted average of the paraffin, naphthene, aromatic (PNA) group properties. However, because of the unconventional nature of the fuel which could be composed of many olefins and oxygenates, the existing methods cannot be applied directly. This paper outlines a methodology to build a model for estimating the n-paraffin, iso-paraffin, olefin, naphthene, aromatic and oxygenate (PIONAOx) composition of any fuel. As an example, a model suited for an ASR-derived GLF was established. Using the present method enables the estimation a fuel reactivity with easy to quantify properties.

The first section explains the methodology, from a general overview to a more precise description of the experimental tests carried out and of the numerical database setting. In the second section, the mathematical formulations behind the pseudo-component properties, and the problem resolution are defined. The third section explores the accuracy of the model compared to the confidence interval of GC × GC measurements for a fuel composition. The precision according to the fuel variability will be investigated in a future work.

## Description of the method

This section first introduces the overall methodology. It then provides more details on the selection of the data and on the performed experimental tests.

### Basis of the method

Since the conventional API (Riazi-Daubert) models [5] were developed to predict the PNA composition of usual fuels, the current work elaborates an overall methodology to build a new model especially adapted to predict the PIONAOx composition of any fuel.

The model was built based on a reference fuel whose composition represents well the studied type of fuel. The model enabled the prediction of the composition of a fuel presenting a similar composition to the reference fuel. The requested degree of similarity between the reference fuel and the studied fuel will be further investigated. An ASR-derived GLF is studied in this paper, therefore two cases are distinguished.

If the studied fuel is an ASR-derived fuel with a composition close to the fuel used as a reference in the present paper, the proposed model could be applied directly and only the fuel properties characterized by the ASTM standard test methods are mandatory to estimate the PIONAOx composition. A further work will study the achieved accuracy with a deviation of the reference fuel composition.

For another type of fuel, the molecular information of a reference fuel has to be defined so the experimental PIONAOx composition and the major components analyzed by GC × GC and gas chromatography-mass spectrometry (GC-MS) respectively are also mandatory to run the whole methodology and create a new model. Then, the model estimates the PIONAOx composition of a fuel similar to the reference with its properties only. Once again, the achieved precision with a deviation of the reference fuel composition needs to be evaluated in a separate study.

The next paragraphs report the principle of the model and the last paragraph refers to the whole methodology.

The model is separated in three steps: retrieving the database, calculating the properties of each hydrocarbon group and resolving an optimization problem to define the composition (Figure 1). More details on each step are given hereafter.

First, the molecule database was created thanks to the software Aspen Properties® and additional relations are used to calculate the missing properties.

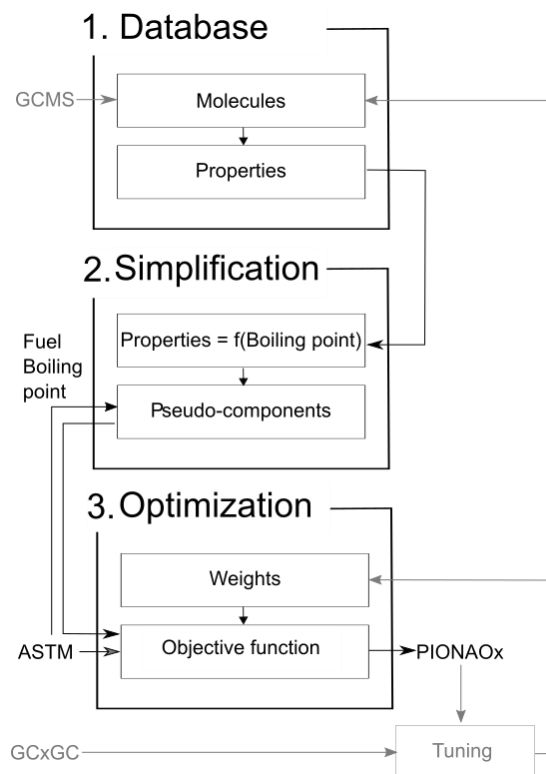


Figure 1. If a model is already set for a studied type of fuel, the fuel properties measured according to ASTM standards are the only inputs needed to calculate the fuel composition. Once the molecule database to represent each hydrocarbon family is set (step 1), the properties of the pseudo-components representing each group can be calculated thanks to the fuel boiling point estimated with ASTM D86 (step 2). Then, the resolution relies of an optimization problem to reduce an objective function based on the difference between the predicted and the real fuel properties pondered with weights to calculate the n-paraffin, iso-paraffin, olefin, naphthene, aromatic, oxygenate (PIONAOx) fractions (step 3). If no model exists for the studied type of fuel, identifying the major molecules present in the fuel (with GC-MS) and knowing a reference composition (with GC × GC) enables the creation of a new model suited for the studied type of unconventional fuel.

Second, the property values used to characterize each hydrocarbon group were calculated. Then, the properties of the fuel were equated as a weighted average depending on the group fractions and on the properties of each group. As the fuel is composed of many molecules, each group was characterized by a single notional molecule, called pseudo-component, to simplify the calculations and to circumvent the impossible experimental identification of all the molecules. A pseudo-component is characterized by its boiling point and by its hydrocarbon group as the properties of the molecules depend on those two characteristics [5].

Last, an optimization problem was solved to minimize the difference between the properties of the mixture of the pseudo-components and the real fuel properties. This resolution gives the hydrocarbon group fractions. Each property does not have the same impact on the calculated fractions, therefore, a weight was allocated to each property in the objective function to change their relative importance. This method offers more flexibility of resolution than the commonly used linear regression [5].

When a new type of fuel is studied, a new model must be set. A fuel is new if its composition is not covered by the range of applicability of the model such as the PIONAOx fractions are badly predicted. The range of applicability will be established in a future study. To set a new model, the composition and the major molecules of the reference fuel are required to run the whole methodology. The structure of the molecules detected by an analysis method, as GC-MS, defined the database. The database and the weights were modified until reaching a good match between the measured and the predicted composition. The group fractions were analyzed experimentally by GC  $\times$  GC. The model was set when the accuracy was considered acceptable.

The first step of the model, i.e. selecting the molecules belonging to the database is described in the next section.

### ***Chemical characterization and chemical database***

This section first describes the experimental methods and their post-processing to characterize the fuel, then, it explains the procedure to build a coherent molecular database to set a model that properly represent the fuel.

#### **Chemical characterization**

Experimental tests were carried out to analyze the fuel composition. Among others, the GC  $\times$  GC enabled the measurement of the PIONAOx composition of the fuel. However, a post-processing of the results was required to deal with an overlapping of the oxygenate molecules and to estimate the confidence interval. The next chapter describes the tests and explains their purpose while the second reports the GC  $\times$  GC post-processing.

#### ***Experimental methods***

The fuel composition must be experimentally characterized for three reasons. First, the major molecules identified in the fuel by GC-MS define the basis of the molecule database. The selection of the molecules is only mandatory to set the model for the first time with a new type of fuel. Secondly, the elemental composition measured with an elemental analyzer (EA) was used as an input property of the optimization problem to calculate the PIONAOx fraction so this analysis is required whenever the model is run. Finally, the hydrocarbon group fractions measured using GC  $\times$  GC coupled with flame ionization detector (FID) must be characterized to enhance the molecule selection and the objective function by defining the best set of weights. This characterization is only required to set the model for the first time.

The results of a GC-MS, an EA, and a GC  $\times$  GC tests realized at the chemical research center CERTECH and at the Laboratory for Chemical Technology of Ghent University are described in the next paragraphs.

One-dimensional GC analysis as GC-MS is commonly used in the industry (ASTM standard test methods D5134 [9], D6729 [10], 6730 [11], D6733 [12], D6839 [13]) as well as in the academic area ([14], [15], [16]). The molecules identified by GC-MS were employed to set the molecule database. Around 0.5  $\mu$ l was directly injected in an apolar column of dimensions 50 m long, 0.25 mm diameter and 0.5  $\mu$ m of film thickness. The blend showed the following typical features regarding the iso-paraffins and the olefins configuration (Table 1). First, the maximal number of substituting -CH<sub>3</sub> is two. Second, the position of the substituting -CH<sub>3</sub> is often located on the second and on the fourth position of the principal chain. Last, the double bond is frequently situated on the first position.

Table 1. Major identified molecules with the GC-MS.

Decane	Benzene
4-methylheptane	Toluene
2,4-dimethylheptane	p-xylene
2-methyl-1-pentene	Ethylbenzene
1-heptene	1-methylethylbenzene
1-octene	1,3,5-trimethylbenzene
2,4-dimethyl-1-heptene	1,2,3-trimethylbenzene
1,2,3-trimethyl-cyclohexane	Styrene
1,3,5-trimethyl-cyclohexane	$\alpha$ -methylstyrene

One-dimensional GC enabled the identification of the molecules in the fuel but suffered of a lack of sensitivity due to co-elution because similar molecules were blended. Then, many constituents were not identified and the molecules cannot be finely sorted into hydrocarbon groups.

GC  $\times$  GC is an improvement developed in 1991 by Liu and Phillips [17] and relies on the GC technique with two capillary columns using different selectivity [18]. The molecules are disassociated according to two different axis to increase the post-processing selectivity.

Although this method is rare compared to one-dimensional chromatography, it is now used in research ([19, 20, 21, 22, 23, 25, 26]) and in industry (standard ASTM UOP990-11 [24]). Jennerwein et al. showed this test method to be more reliable for modern and complex fuels because of a higher sensitivity [25].

The GC  $\times$  GC analysis was performed using an apolar column (Rxt-1 PONA, 50 m long, 0.25 mm internal diameter, 0.5  $\mu$ m film thickness) and a mid-polar column (BPX-50, 2 m long, 0.15 mm internal diameter, 0.15  $\mu$ m film thickness) heated from 0°C to 250°C at a heating rate of 3°C/min. Further information as the sample preparation and the method description are detailed in an article by Dijkmans et al. [19].

The components were quantified by averaging three GC  $\times$  GC-FID analyses and their identification was performed via GC  $\times$  GC-time of flight (TOF)/mass spectrometry (MS) analysis (see Table 2). GC  $\times$  GC analyzes the whole fuel composition, including naphthenoaromatics, diaromatics, nitrogenates and sulfurates whereas the current method only focuses on the PIONAOx fractions. The calculated and the measured fractions must be compared on a same basis. Therefore, the whole fuel composition was simplified into a PIONAOx composition with the following procedure. The measured naphthenoaromatics were equally distributed between the naphthenes and the aromatics, the diaromatics were considered as monoaromatics, and the nitrogenates and the sulfurates were neglected.

Table 2. Hydrocarbon group repartition.

Chemical group	% wt/wt
Olefin	31.09
Monoaromatic	28.39
Mononaphthene	14.18
Iso-paraffin	12.38
Oxygenate	6.66
n-paraffin	5.47
Naphthenaromatic	1.11
Nitrogenate	0.66
Diaromatic	0.04
Sulfurate	0.02
Total	100

Three GC × GC analyses using nitrogen chemiluminescence detector (NCD) and sulfur chemiluminescence detector (SCD), i.e., GC × GC-NCD and GC × GC-SCD, were realized to measure an average nitrogen and sulfur content. An EA was also used to compare and validate the carbon, hydrogen, and oxygen contents (Table 3).

Table 3. Fuel elemental composition.

Atom	% wt/wt	Method
Carbon	84.58	EA
Hydrogen	12.76	EA
Oxygen	2.34	EA
Nitrogen	0.26	GC × GC-NCD
Sulfur	0.06	GC × GC-SCD

The oxygen content measured by an EA was compared with the one calculated from the number of oxygen atoms in the molecules identified by GC × GC-FID and GC × GC-TOF/MS. A difference was observed, due to the overlap of the oxygen signal. Consequently, a correction, presented in the next paragraph, was applied. The experimental random error is also presented in the following part by the mean of a confidence interval calculation.

### GC×GC post-processing

A difference between the amount of oxygen atoms measured by GC×GC and by the EA was observed. After having explained this difference, a correcting factor was introduced to estimate a corrected oxygenate fraction. Then, the whole fuel composition was known which allowed to estimate the confidence interval.

If a hydrocarbon group is several orders of magnitude more concentrated than another group whereas their similarity regarding to the columns selectivity is too high, the peak signal of the first group will hide the peak of the second group. The identification of oxygenates is still a challenge with GC × GC because oxygenates overlap with monoaromatics, diaromatics, triaromatics, naphthenoaromatics and naphtheneodiaromatics [19, 26]. In the present study, the oxygenates overlapped with the monoaromatics.

A correction was applied to estimate the amount of overlapped oxygenates that cannot be identify with GC × GC. This correction relies on an EA to relate the real amount of oxygen in the fuel with the amount of oxygen in the identified molecules that did not suffer

of the overlapping. The hypothesis adopted to perform this correction are described in the next paragraph.

The oxygen content analyzed with the EA and the amount of the overlapped oxygenate molecules are tied together with the oxygen-to-carbon mass fraction (OC), the hydrogen-to-carbon mass fraction (HC) and the molar mass (Mm) of two types of molecules (the firsts being all the molecules in the fuel and the seconds being the overlapped molecules). Therefore, the type of molecules, which drives the OC and HC, and the size of the molecules are mandatory. Usually, monoaromatics overlap with aliphatic ketones [26] so the overlapped oxygenate molecules were considered as aliphatic ketones. The identified molecules with GC × GC were mainly ketones and alcohols. They have the same OC and a similar HC so both ratios of the overlapped oxygenates and the identified oxygenate molecules were considered equal. The number of carbon atoms of the overlapped oxygenate is discussed in a second step. As no information were available, the molecules were supposed similar in size with the identified oxygenate fraction. Then, the OC, the HC and the size of the overlapped oxygenate were esteemed similar with those of the identified oxygenates. Therefore, the proportionality between the oxygenate molecules and the oxygen atomic content observed with GC × GC were considered respected with the EA. Then, under this hypothesis, a corrected response volume defined by the following equation was introduced to estimate the overlapped volume of oxygenate molecules:

$$V_{O_c} = \frac{OC_{EA}}{OC_{GC \times GC}} V_O, \quad (1)$$

where  $OC_{EA}$  and  $OC_{GC \times GC}$  are the oxygen-to-carbon fractions measured with the EA and with the GC × GC respectively. The oxygen content calculated from the molecules identified by GC × GC-FID and GC × GC-TOF/MS is 56.4% lower than the oxygen fraction measured with the EA (Table 3).

A corrected volume was also introduced to calculate the overestimated concentration of aromatic compounds due to the overlapping. However, the overlapping concerns the measured volume peaks which are not equal to the real volume peaks reported in equation 1. They were given by a response factor (RF) defined by:

$$RF_g = \frac{V_g}{V_{g_m}}, \quad (2)$$

where  $g$  refers to the group and  $m$  to the measurement. This factor RF is different for each molecule but strongly depends on the group (Table 4). Therefore, an averaged response factor was used for each group. The overlapped oxygenate being considered as aliphatic ketones, the factor range of the overlapped oxygenates is equal to the range of aliphatic ketones.

Table 4. Response factors (RF) [27, 28].

Chemical group	RF range	Averaged RF
Monoaromatics	[0.81; 0.85]	0.83
Aliphatic ketones	[1.00; 1.20]	1.10

Then, the overlapped measured volume of oxygenates  $V_{O_{m,c}} - V_{O_m}$  was subtracted to the measured aromatic volume peak  $V_{A_m}$ , giving the corrected volume  $V_{A_{m,c}}$ :

$$V_{A_{m,c}} = V_{A_m} - (V_{O_{m,c}} - V_{O_m}). \quad (3)$$

Once the corrected real volume peak of the aromatics  $V_{A_c}$  was deduced from  $V_{A_{m,c}}$  and the averaged response factor  $RF_A$  (Table 4), the corrected fractions and the confidence intervals could be evaluated.

Three experimental test runs were realized to calculate a confidence interval at 95% of the PIONAOx averaged values. The standard deviation of the mean value was given by the standard deviation of the measured values and by the number of runs led with the GC  $\times$  GC (3 in this study). The average fractions  $\bar{Y}_g$  were normalized to be expressed in percentage  $Y_g$  (Table 5). This last calculation is equivalent of applying a scale factor which was used to get the standard deviation of the mean value of the normalized fractions. This deviation gave the confidence interval of the mean value at 95% by applying the Student's distribution for an estimated variance and a low number of run (Table 5).

Table 5. Normalized mean value and confidence intervals (CI) of the PIONAOx fractions (%wt/wt).

Chemical group	$Y_g$	CI
n-paraffin	5.4	[5.1;5.7]
iso-paraffin	12.2	[11.6;12.9]
Olefin	30.8	[28.9;32.6]
Naphthene	14.6	[14.0;15.2]
Aromatic	24.4	[23.4;25.4]
Oxygenate	12.6	[12.5;12.7]

## Chemical database

A chemical database was created to calculate the mean properties of each hydrocarbon group. A new database must only be created if a fuel whose most representative molecules and whose composition are very different from the one studied in this paper. The following criteria must be respected to select molecules representing correctly each PIONAOx hydrocarbon group in the studied fuel.

1. The ranges of the hydrocarbon group boiling points must contain the fuel Mean average boiling point (MeABP). When several isomer sub-groups are selected in a single hydrocarbon group to consider isomers, their boiling point ranges must be similar such as the sub-groups are all equally represented over the whole boiling point range.
2. For each sub-group of each hydrocarbon family, four molecules were selected to rely on a smooth group representation.
3. The selected isomer forms must have a quite similar structure to avoid a too wide distribution of the properties of each group database which could lead to a pseudo-component featuring properties much different from its representative group.

4. To rely on a relevant database, the molecules were selected based on the results of the GC-MS analysis and on the predominant molecules produced during the decomposition of the most current polymers used in the automotive industry [6, 29].

The consequences of the four previous rules on the molecules selected to build the model for an ASR-derived fuel are described in the next paragraphs. They refer only to the fuel studied in the present paper but a similar logic could be applied to any fuel.

**n-paraffin (P).** As no isomers exist for n-paraffin, only one molecule per number of carbon atom was selected. The boiling point rules impose the selection of molecules with a number of carbon atoms from 7 to 11.

**Iso-paraffin (I).** Iso-paraffins can be substituted with several  $-CH_3$ . Primary carbons are more likely to be present in the ASR fuel because usual polymers used in the automotive industry present only one substituting  $-CH_3$  on each carbon atom as in polypropylene (PP) or ethylene propylene diene monomer (EPDM). Based on the GC-MS analysis, molecules with a higher number of substituting  $-CH_3$  than two were not selected. Moreover, the boiling point range is the same for each sub-group such as the lowest number of carbons in the principal branch of the bi-substituted alkanes is five. The position of the substituting  $-CH_3$  was set preferentially at the second and at the fourth position according to the GC-MS analysis. The substitutes of mono-substituted paraffins are only at the second position because the database of Aspen Properties<sup>®</sup> does not include all the paraffins substituted at the fourth position. Mono and bi-substituted paraffins ranging from C7 to C10 were selected.

**Olefin (O).** Olefins can be straight or branched so both sub-groups were considered. According to the GC-MS analysis, the position of the double bond tends to be located at the first position and, similarly to the iso-paraffins, one to two substituted  $-CH_3$  can be located at the positions 2 and/or 4, i.e. alpha and/or gamma position. If the Aspen Properties<sup>®</sup> database did not include a requested molecule, another molecule – considered equivalent – with a different double bond position and with one or two substituting  $-CH_3$  located at the alpha and gamma positions was selected. As for the iso-paraffin case, mono-substituted olefins were only substituted at the second position because the Aspen Properties<sup>®</sup> database does not include the fourth position substituted 1-olefins or their equivalents. An exception was made with the selection of 2,5-dimethyl-4-octene which is the only available bi-substituted octene-based molecule in Aspen Properties<sup>®</sup>. No diene olefins were selected because their properties show major differences and they were not analyzed by GC-MS (Table 1).

**Naphthene (N).** According to the results of the GC-MS, naphthenes were selected on a cyclohexane basis with three substituting  $-CH_3$ . In order to cover a wider range of boiling points, molecules with a substituting chain containing 1 to 3 carbon atoms were added. The bi-substituted 1,1-dimethylcyclohexane was also included in the model to consider the possibility to face a di-substituted carbon. Those different types of naphthenes were found during the polystyrene (PS) decomposition [30].

**Aromatic (A).** Acrylonitrile butadiene styrene (ABS) decomposition produces a high quantity of styrene,  $\alpha$ -methylstyrene and iso-propylbenzene [29] while polyurethane (PUR) induces high amounts of alkylbenzenes. The molecules were selected assuming only mono-substituted carbons. Alkylbenzenes with a number of carbon atoms ranging from 6 to 10 were selected.

**Oxygenate (Ox).** The model was based on 1-alcohols and 3-ketones with a number of carbons from 3 to 6 and from 5 to 8 respectively. The hydroxyl group was set at the first position because 1-alcohols are usually used in the pseudo-component technique [5] while 3-ketones are well-described in the software Aspen Properties®.

The proposed database (Table 6) may be suitable for a wide number of ASR-derived gasoline-like fuel but a deeper study investigating the accuracy of the method with a variation of the reference fuel composition could validate that hypothesis.

Table 6. Molecular database.

Molecule	Group	Boiling point (°C)
n-heptane	n-paraffin	98.43
n-octane	n-paraffin	125.68
n-nonane	n-paraffin	150.82
n-decane	n-paraffin	174.16
2-methylhexane	Iso-paraffin	90.05
2-methylheptane	Iso-paraffin	117.65
2-methyloctane	Iso-paraffin	143.30
2-methylnonane	Iso-paraffin	167.00
2,4-dimethylpentane	Iso-paraffin	80.49
2,4-dimethylhexane	Iso-paraffin	90.43
2,4-dimethylheptane	Iso-paraffin	132.50
2,4-dimethyloctane	Iso-paraffin	155.90
Methylcyclohexane	Naphthene	100.93
Ethylcyclohexane	Naphthene	131.79
n-propylcyclohexane	Naphthene	156.75
1,1-dimethylcyclohexane	Naphthene	119.55
1,2,3-trimethylcyclohexane	Naphthene	151.08
1,3,5-trimethylcyclohexane	Naphthene	140.55
1-heptene	Olefin	93.64
1-octene	Olefin	121.26
1-nonene	Olefin	146.87
1-decene	Olefin	170.60
2-methyl-1-hexene	Olefin	91.84
2-methyl-1-heptene	Olefin	119.22
2-methyl-1-octene	Olefin	144.65
2-methyl-1-nonene	Olefin	168.40
2,4-dimethyl-1-pentene	Olefin	81.59
2,4-dimethyl-1-hexene	Olefin	110.79
4,6-dimethyl-2-heptene	Olefin	129.87
2,5-dimethyl-4-octene	Olefin	153.48
Benzene	Aromatic	80.09
Toluene	Aromatic	110.63
n-ethylbenzene	Aromatic	136.20
n-propylbenzene	Aromatic	159.24
Styrene	Aromatic	145.16
α-methylstyrene	Aromatic	165.50
Propan-1-ol	Oxygenate	97.20
Butan-1-ol	Oxygenate	118.75
Pentan-1-ol	Oxygenate	137.75

Hexan-1-ol	Oxygenate	156.75
3-pentanone	Oxygenate	101.99
3-hexanone	Oxygenate	123.50
3-heptanone	Oxygenate	147.40
3-octanone	Oxygenate	167.50

## Selection and characterization of the properties

After having described how the properties currently used in other methods can be adapted to the new methodology, the experimental tests performed to characterize the properties according to a reproducible ASTM method are reported, followed by the listing of the property database sources.

### Selection of the properties

This section first fixes the needed number of properties and then describes the properties selected to calculate the PIONAOx fractions. This step is not mandatory to run or create a model.

Although an optimization problem was solved rather than relying on a linear resolution as in conventional methods [5], the number of properties was determined as if the resolution was depending on a degree of freedom. Six compositional groups must be predicted, so five properties and one additional constraint (sum of the fraction equal to one) were first tested. However, better results were obtained with the same five properties and constraint, and with the OC ratio as a sixth property.

Two criteria should be met to select the six properties. First, the values of the properties included in the model must be strongly dependent on the hydrocarbon group. Conversely to the existing methods, this criterion was facilitated in the present study thanks to the pseudo-component method that enabled the dependency of the properties on the boiling point to be put aside. In the existing methods, the measured properties were not always used in the equations but were included in the calculation of another property - which was integrated into the system - especially created in purpose. However, calculations could create error propagations, so the second criterion is the selection of measured properties instead of calculated properties. The first criterion prevails. Properties respecting the first criteria are already known thanks to the existing methods to predict the PNA fractions. The API (Riazi-Daubert) [5] method proposed several systems of equations operating with different properties which depend on the hydrocarbon group and are quite constant over the boiling point range. However, some properties are the results of a calculation between two other measured properties which is opposed to the second criteria. In this case, the measured properties were used as candidates instead of the one resulting of the calculation. A candidate was accepted if the measured property validates the first criteria. The upcoming properties were adopted.

### Specific Gravity

The specific gravity (SG) was defined by comparing the fuel and the water densities at 15.5°C:

$$SG = \frac{\rho_{\text{fuel},15.5}}{\rho_{\text{water},15.5}} \quad (4)$$

where  $\rho_{\text{fuel},15.5}$  and  $\rho_{\text{water},15.5}$  are the fuel density and the water density at 15.5 °C respectively.

The SG is linked with the length of the intermolecular and intramolecular bonds in the fuel blend. This parameter is clearly dependent on the hydrocarbon group and is a simple property which can be used in this method.

### Refractive index

Conventional methods rely on the refractivity intercept ( $R_i$ ) or on the  $m$ -parameter. The  $R_i$  was created because the refractive index against density for each hydrocarbon group is linear [5]:

$$R_i = n_{20} - \frac{\rho_{20}}{2} \quad (5)$$

where  $n_{20}$  and  $\rho_{20}$  are the refractive index and the density of the studied molecule at 20 °C.

For each type of chemical group, the refractive index is inversely proportional to the  $Mm$ . Then, the  $m$ -parameter is also a good hydrocarbon group indicator [5]:

$$m = Mm(n_{20} - 1.475), \quad (6)$$

The refractive index  $n_{20}$  is not the result of a calculation so it respects the condition 2 previously evoked whereas  $R_i$  and  $m$  do not. Moreover, the refractive index allows to separate the group fractions for a given boiling point (condition 1). Therefore, the refractive index at 20°C was selected.

### Viscosity gravity function

The viscosity gravity function (VGF) was proposed for fuels with a kinematic viscosity at 38°C ( $v_{38}$ ) lower than 3.6 cSt, which are typically light fractions, on the observation that the plot of the SG against  $\ln(v_{38})$  is linear for each hydrocarbon group [5]:

$$VGF = -1.816 + 3.484 SG - 0.1156 \ln(v_{38}). \quad (7)$$

$\ln(v_{38})$  and  $v_{38}$  do not respect the previous condition 1 so the VGF was preferred.

### Watson K factor

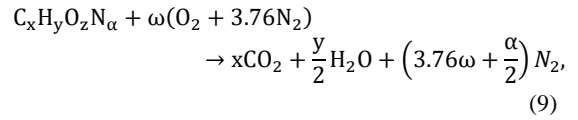
The Watson K factor ( $K_w$ ) defined in Bergamn's method is widely used to characterize fuels ([5, 31]):

$$K_w = \frac{1.8 T_b^{1/3}}{SG}, \quad (8)$$

where  $T_b$  is the normal boiling point for a pure component and the MeABP for a mixture. The  $K_w$  coefficient was developed to identify the type of molecules in a fuel blend so it is highly related to the chemical family. The boiling point and the SG are indeed a consequence of the strength of the chemical bonds. The MeABP does not respect the previous condition 1 so it cannot substitute the  $K_w$ .

### Air-to-fuel ratio under stoichiometric conditions ( $AF_s$ )

The HC ratio used in the existing methods [5] represents well the hydrocarbon groups but the air-to-fuel ratio under stoichiometric conditions ( $AF_s$ ) was preferred to consider the oxygen content. It is defined by the global equation of combustion of the generic fuel  $C_xH_yO_zN_\alpha$  under stoichiometric conditions and when the combustion is complete and where nitrogen is supposed to react into  $N_2$ :



where  $\omega$  is the needed number of moles of oxygen to burn the fuel under stoichiometric condition and is defined as:

$$\omega = x + \frac{y - 2z}{4}. \quad (10)$$

The  $AF_s$  depends on the stoichiometric mole number of air which can be calculated from the atomic weight ratio obtained from the atomic weight fractions:

$$AF_s = \frac{1}{Mm_c} \left( \frac{1 + \frac{(HC_w \frac{Mm_c}{Mm_H} - 2OC_w \frac{Mm_c}{Mm_O}) (Mm_{O_2} + 3.76Mm_{N_2})}{4}}{1 + HC_w + OC_w + NC_w} \right), \quad (11)$$

where  $Mm_A$  is the  $Mm$  of atom A and the weight ratio between atom A and carbon,  $AC_w$ , is deduced from the atomic mass fractions:

$$AC_w = \frac{y_A}{y_C}. \quad (12)$$

where  $y_A$  refers to atom A and  $y_C$  refers to carbon.

### OC weight fraction

The oxygen-to-carbon mass fraction (OC) was included to handle the oxygen composition because using the air-to-fuel ratio enabled the oxygen content within the fuel to be considered but did not allow the setting of the oxygen composition.

Once the relevant properties are selected, the methods to characterize the properties of the real fuel and of the molecules belonging to the database can be defined.

## Characterization of the properties

The experimental test methods and the calculations to define the real fuel properties will be presented, followed by the sources and the calculations of the properties included in the database.

### Properties of the real fuel

The experimental characterization of the fuel properties is the only mandatory input to run an existing model to calculate the PIONAOx composition. However, as the model development is based on a given reference fuel, the obtained precision must be calculated depending on the variation of the reference fuel composition. This will be studied for an ASR-derived GLF in a future work. If the model is not yet developed, the measurements of the properties must be coupled to the chemical analysis of the reference fuel. In the present study, the properties were characterized thanks to the ASTM standard test methods listed in Table 7 except for the nitrogen and sulfur fractions that were measured using GC × GC-NCD and GC × GC-SCD at Ghent University. Using a GC × GC to analyze the nitrogen and sulfur content is a special feature of the current work but the model

can be run only relying on analysis lead by standardization companies, with GC-FID, GC-NCD, GC-SCD or EA. Depending on the type of fuel, several standard test methods can be applied as, for a light fuel, ASTM D4808 for hydrogen, ASTM D5623 for a sulfur concentration range from 0.1 to 100 mg/kg, ASTM D5762 for a nitrogen level of 40 µg/g to 10 000 µg/g, and ASTM D5622 for an oxygen mass content from 1.0% to 5.0%. ASTM D5291 is not recommended for O, N and S because the results are less accurate.

The MeABP was calculated from the volume average boiling point (VABP) [5] obtained by the volumetric distillation curve measured experimentally according to the standard test method ASTM D86 [32]:

$$VABP = \frac{T_{10} + T_{30} + T_{50} + T_{70} + T_{90}}{5}, \quad (13)$$

where  $T_p$  (expressed in Kelvin) is the temperature at which  $p\%$  of the fuel is the evaporated. The VABP was converted into the MeABP [5]:

$$MeABP = VABP + \Delta_{Me}, \quad (14)$$

where the shifting coefficient  $\Delta_{Me}$  is defined as [5]:

$$\ln(\Delta_{Me}) = -1.53181 - 0.0128(VABP - 273.15)^{0.6667} + 3.646064SL^{0.333} \quad (15)$$

and SL is the 10-90 slope defined by [5]:

$$SL = \frac{T_{90} - T_{10}}{80}. \quad (16)$$

The experimental methods to measure all the fuel properties are listed in Table 7.

Table 7. Fuel properties and methodologies.

Property	Value	Unit	Method
$\rho$ at 15.5°C	796.1	kg/m <sup>3</sup>	ASTM D4052
$v$ at 40°C	0.6615	cSt	ASTM D445
C	84.58	%wt/wt	ASTM D5291
H	12.76	%wt/wt	ASTM D5291
O	2.34	%wt/wt	ASTM D5622
N	0.26	%wt/wt	GC × GC-NCD
S	0.06	%wt/wt	GC × GC-SCD
$n$ at 20°C	1.4419	/	ASTM D1218
SG	0.7969	/	Equation 4
VGF	1.008	/	Equation 7
Kw	11.412	/	Equation 8
MeABP	144.9	°C	ASTM D86; Equation 14

### Properties of the molecules belonging to the database

The properties of the real fuel were related with the properties of the molecules in the hydrocarbon group. A property database, erected from the library of the software Aspen Properties®, was built to represent each group. This section first lists the molecules included in the software and then cites the formulas to estimate the missing properties. Finally, the properties of each chemical group were plotted to check the distribution over the map.

The Mm, the boiling point, the SG and the refractive index were directly extracted from the database of Aspen Properties® except for the refractive index of 2,4-dimethylheptane, 1,2,3-trimethylcyclohexane, 1,2-dimethyl-1-pentene, 1,2-dimethyl-1-hexene, 4,6-dimethyl-2-heptene, and 2,5-dimethyl-4-octene. The refractive indices of the last molecules were calculated thanks to the refractive index parameter I [5]:

$$n = \frac{1 + 2I}{(1 - I)^2} \quad (17)$$

which can be evaluated with an accuracy of 0.5% for a Mm range from 70 to 300 [5]:

$$I = 2.343 \cdot 10^{-2} \exp(T_b + 2.468 SG - 1.026 \cdot 10^{-3} T_b SG) T_b^{0.0572} SG^{-0.72}. \quad (18)$$

All the missing properties were evaluated with Aspen Properties® using the PENG-ROB base property method [33]. The Watson K factor was calculated with equation 8.

Once the database was entirely defined, the property distribution over the boiling point range was plotted to ensure a good separation between the groups. This differentiation is good, except in the following cases (Figures 2a, 2b, 2c, 2d, 2e and 2f).

1. The iso and normal paraffin share part of their ranges.
2. The refractive index of the oxygenate group overlaps with the iso and normal paraffins.
3. The AF<sub>s</sub> of olefins and naphthenes are the same over the boiling point range.
4. The AF<sub>s</sub> of iso and normal paraffin are the same over the boiling point range.

The pseudo-component method helped to distinguish locally the properties for the first and the second cases and the OC allowed to estimate the oxygenate content.

This first section described the methods to build the database to create or to run a model. The next part will develop the calculations included in the core of the model.



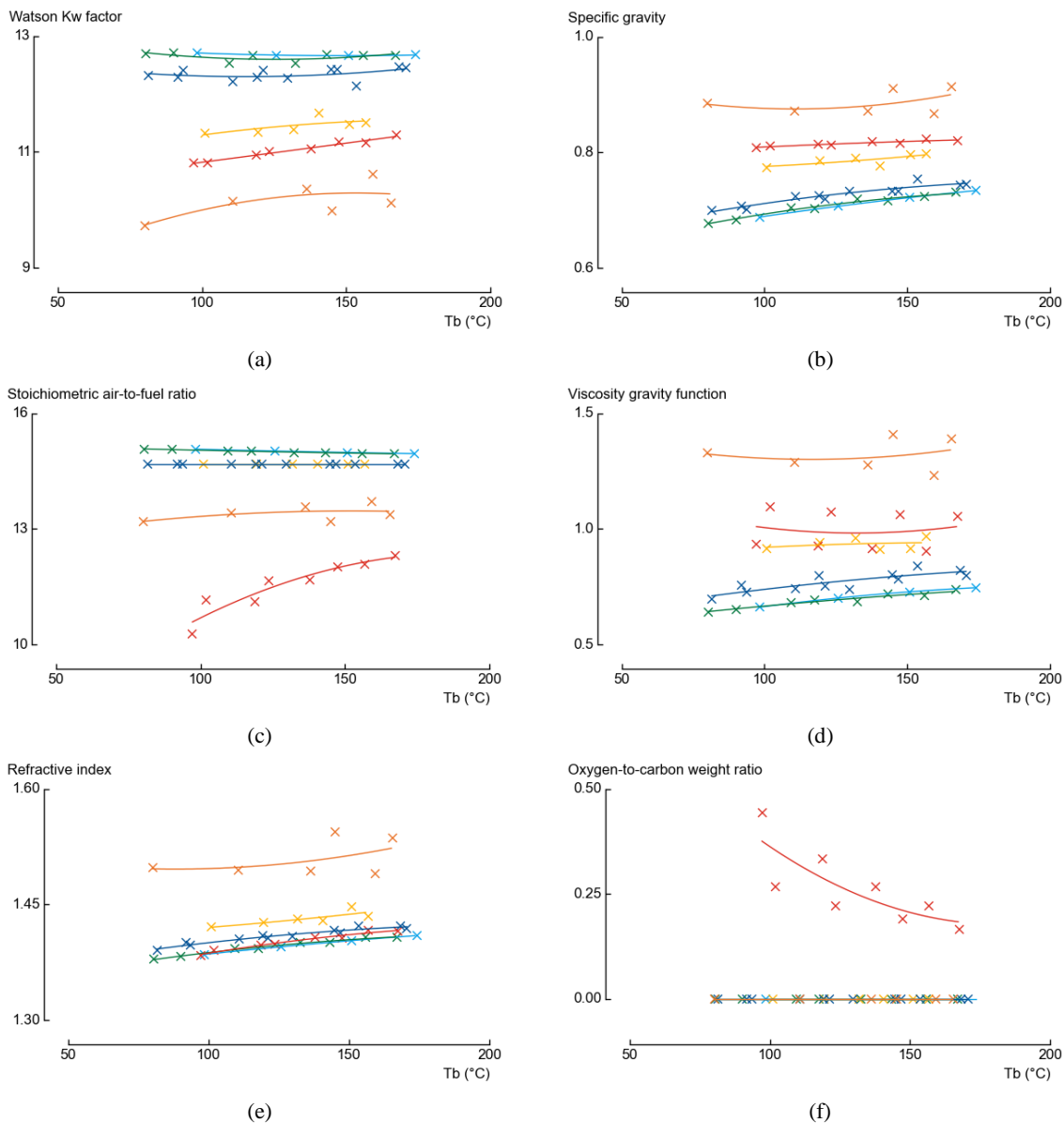


Figure 2. Dependency of the six chosen fuel properties on the hydrocarbon group. The cross refers to the molecules included in the database and the lines are the results of a second order polynomial regression for each hydrocarbon group. Light blue: n-paraffin, green: iso-paraffin, dark blue: olefin, yellow: naphthene, orange: aromatic, red: oxygenate.

## Mathematical models and resolution

This section presents the formulas to build the pseudo-components – reduced number of theoretical molecules representing a given hydrocarbon group – thanks to a molecule database that characterizes well the molecules in the fuel. Then, the section explains the procedure to approximate the composition of an unconventional fuel thanks to a relation involving its properties measured by standard test methods.

### *Pseudo-component definition*

A complex fuel composed of hundreds of molecules can be represented thanks to its pseudo-components. This section develops the equations defining the properties of the pseudo-components.

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A pseudo-component is a notional molecule belonging to a hydrocarbon group and characterized by its boiling point. Therefore, each hydrocarbon group in a fuel can be represented by one or several pseudo-components depending on the 10-90 slope SL (equation 16). If SL is lower than 0.8, the narrow boiling range hypothesis is respected and one pseudo-component per group is sufficiently accurate to study the fuel. Otherwise, the fuel boiling point range is subdivided and several pseudo-components representing each division must be determined [5]. In the present study,  $SL = 0.745$  so the narrow boiling range is respected. This simple definition allowed to calculate the properties of each hydrocarbon group using only two inputs: the MeABP of the fuel and a database of molecules for each group. The database was used as a basis to define equations for each studied property.

The equations were built from the observation that the correlation coefficients (R) between the calculated properties from a second order polynomial regression and the properties from the database are higher than 0.94, except for the Watson K factor of the 2-methylakane group (R = 0.83). Therefore, the property versus the boiling temperature for a same subgroup of isomers in a chemical group is close to be quadratic. The properties of the pseudo-components were based on a second order regression. The rules to select the molecules belonging to each hydrocarbon group defined in the first section enabled the different isomers to not be favored during the polynomial regression. The second order polynomial is of the form:

$$P_{p,g}(T_b) = a_{p,g} + b_{p,g}T_b + c_{p,g}T_b^2, \quad (19)$$

where  $P_{p,g}$  is the function defining the property  $p$  of the hydrocarbon group  $g$  depending on the boiling point value  $T_b$ . For each property and each group, the curves must be located within the property range of the sub-groups. This condition was validated in the current study (see Figures 2a, 2b, 2c, 2d, 2e and 2f).

The properties of each pseudo-component are equal to  $P_{p,g}(\text{MeABP})$  and approximate the properties of the mixtures of the molecules belonging to each hydrocarbon group. Therefore, the fuel properties were calculated with:

$$P_p = \sum_g y_g P_{p,g}, \quad (20)$$

where  $P_{p,g}$  is the  $p$ -th property of the pseudo-component characterizing the  $g$ -th group and  $y_g$  is the mass fraction of the  $g$ -th group.

The pseudo-components helped to decorrelate the fuel properties according to the different groups. This enabled the creation of the equations linking the fuel properties and the group fractions. The resolution relied on an optimization problem and is described in the next section.

## Resolution

After explaining the benefits of minimizing an optimization problem compared with the linear resolution adopted in conventional methods [5], the details on the minimized objective function are reported.

In the present study, n-paraffin, iso-paraffin and olefin showed very similar ranges of values. Moreover, the boiling point and the properties of the molecular mixtures of each hydrocarbon group in the fuel will not precisely be equals to those of their representative pseudo-component. Because the ranges overlap, these differences of boiling point and properties will propagate an error on the calculated fractions. Consequently, to take into account the inaccuracies due to the differences between the molecular mixtures and the pseudo-components, an optimization problem was solved to introduce a higher flexibility than a simple linear resolution.

If a model already exists for the studied fuel, only one optimization problem must be solved in order to reduce the difference between the  $p$ -th property of the real fuel,  $P_{\text{rf},p}$ , and the  $p$ -th property of the mixture of the pseudo-components,  $P_p$ . The  $p$ -th decision variable was defined as:

$$f_p = \frac{|P_p - P_{\text{rf},p}|}{P_{\text{rf},p}}. \quad (21)$$

The properties of the mixture of the pseudo-components  $P_p$  were calculated according to equation 20.

Weight coefficients were introduced in the objective function to couple the properties with a relative influence:

$$O_p = \sum_p w_p f_p, \quad (22)$$

where the weight coefficients  $w_p$  were equal to a power of 10.

The objective function  $O_p$  was reduced thanks to the matlab `fmincon` function included into the GlobalSearch object coupled with the MultiStart algorithm to run several start points uniformly distributed. Two constraints were also set, the resolution domain [0;1] and:

$$y_p + y_i + y_o + y_n + y_a + y_{Ox} = 1. \quad (23)$$

To build a model suited for a new type of fuel, a second optimization problem was solved which will give the values of the weights  $w_p$ . The best set of weights was obtained when the difference between the calculated fuel fractions and the measured fractions of the reference fuel was minimized. The reference fuel must be a good representative of the studied type of fuel in terms of molecules and group fractions. The mathematical formulation of the objective function is:

$$O_g = \sum_g w_g f_g, \quad (24)$$

where the decision variables  $f_g$  are defined as the difference between the calculated mass fractions  $y_g$  obtained by minimizing the objective function  $O_p$  defined by equation 22 and the normalized average value  $Y_g$  of the measured fractions of each group  $g$ :

$$f_g = |y_g - Y_g|. \quad (25)$$

No priority was set such as the weights  $w_g$  were all set equal to one. The minimization of  $O_g$  gave the weights  $w_p$ . The number of starting points defined in the GlobalSearch object was fixed by trial and error when the returned set of weights  $w_p$  was persistent.

The entire methodology to develop a model which predict the PIONAOx composition of an unconventional fuel was proposed. The model depends on two parameters which are the molecule database (Table 6) and the weights defining the objective function (equation 22). Those parameters were defined according to a reference fuel which represents well the type of studied fuel. Some molecules of the database were removed and several set of weights were tested to investigate the achieved accuracy with different parameters. The model will be afterwards run to estimate the composition of another fuel presenting features which are close to the reference fuel. However, although the accuracy was increased when the parameters

were tuned with the reference fuel, it may be decreased for the other studied fuel. A high parameter tuning is expected to decrease the maximal variation of composition which is correctly handled. Therefore, the last section aims at estimating which parameters allow to achieve an acceptable accuracy with the reference fuel. The precision of the model with other fuels than the reference one will be investigated in a future study. This will define the maximal composition variation allowed to rely on the same model than the one developed with the reference fuel.

## Results and discussion

The model depends on two parameters, the first is a molecule database representing each hydrocarbon group of a reference fuel characterizing the studied type of fuel. The second is the set of weights impacting the reduction of the objective function during the resolution step. The accuracy of the model was investigated for several parameter settings. Several molecule databases were first created with all the weights assigned to each property  $w_p$  equal to one, then several set of weights were tested with a selection of the most interesting molecule databases.

### Tuning of the molecule database

The molecules listed in Table 6 creates an extended database where the isomers are equally represented for each boiling point. However, the molecular configuration depends on the production process such as the type of predominant molecules depends on the boiling point. Tuning the initial molecule database listed in Table 6 is a way to match the fuel and increase the accuracy of the model. The refinement was performed with respect of the following rules:

1. The selected molecules still cover the PIONAOx groups.
2. The ranges of the hydrocarbon group boiling points must contain the fuel MeABP. For each hydrocarbon group, at least three molecules were selected to rely on a second order polynomial regression.
3. For each property and each group, the plot of the second order polynomial function must be located within the property range of the isomer sub-groups of the original database.

To monitor the evolution of the accuracy along the refinement, the molecule tuning scale is defined as:

$$S_m = \frac{n_{refine}}{N_{refine}}, \quad (26)$$

where  $N_{refine}$  is the number of molecules removed from the initial molecule database listed in Table 6 to reach the highest accuracy with all the weights equal to one and  $n_{refine}$  is the progress variable defined by the number of molecules removed to reach the current studied error. The molecule tuning scale evolves according to the number of removed molecules from the initial database.

The molecules were removed in a precise order depending on the following automatic reduction sequence. The molecules were tested per group in the following order: aromatic, oxygenate, naphthene, olefin, iso-paraffin. This order was selected to respect the group repartition order – from higher to lowest and inversely – of half of the

studied properties (the Watson K factor, the specific gravity and the viscosity gravity function) that appears when the properties are plotted (see Figure 2). This avoids a bad interaction between the  $(n+1)$ -th removed molecule and the  $n$ -th removed one. For instance, the aromatics have only one neighbor group – the oxygenate (Figures 2a, 2b, 2d) – so these molecules are mostly only impacted by the oxygenates. Therefore, the deletion of an aromatic molecule could be inhibited by the first deletion of an oxygenate without any possible counterbalance by a second group to have a second opportunity to remove the aromatic. No n-paraffin was deleted because only 4 molecules belong to the original database. At each step, the selected molecule is the one whose deletion reduced the most the error of its hydrocarbon group. After one reduction sequence, 9 molecules were removed, reducing the global error (Figure 3).

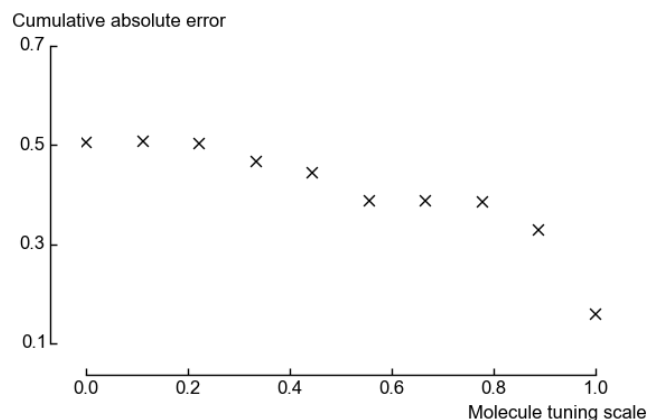


Figure 3. Absolute cumulative error along the molecule refinement.

A group-per-group molecule refinement following this order was obtained: aromatic, naphthene, olefin, iso-paraffin (Table 8). No oxygenates were removed from the original database.

Table 8. Order of the molecular refinement.

Iteration	$S_m$	Molecule name	Hydrocarbon group
1	0.11	Propylbenzene	Aromatic
2	0.22	Toluene	Aromatic
3	0.33	1,2,3-trimethylcyclohexane	Naphthene
4	0.44	1,1-dimethylcyclohexane	Naphthene
5	0.55	2-methyl-1-heptene	Olefin
6	0.66	2,4-dimethylheptane	Iso-paraffin
7	0.77	2,4-dimethyloctane	Iso-paraffin
8	0.88	2-methylnonane	Iso-paraffin
9	1	2-methyloctane	Iso-paraffin

The best accuracy was reached at a molecule tuning scale of one with a cumulative absolute error of 16 % (Figure 3). For each group, the error is further decreased when the confidence interval is considered ( $\epsilon_{CI} < 1\%$  except for monoaromatics and n-paraffins for which it is still acceptable, Table 9). The cumulative absolute error reaches 12.6 % when the confidence interval is considered.

Table 9. Estimated fractions  $Y_e$  (% wt/wt) and absolute errors from confidence interval comparison ( $\epsilon_{CI}$ , %) at a molecule tuning scale equal to 1.

Chemical group	$Y_e$ (% wt/wt)	$\epsilon_{CI}$ (%)
n-paraffin	0.3	4.8
iso-paraffin	11.2	0.4
Olefin	30.1	0
Mononaphthene	13.4	0.5
Monoaromatic	32.1	6.7
Oxygenate	12.8	0.1

Increasing the molecule tuning scale has the benefit to improve the accuracy when the model is being set with the reference fuel. Then, the objective being to apply this model to another fuel similar to the reference fuel, the accuracy may decrease and the range of applicability of the model could drop due to the differences with the reference fuel. Therefore, to relax this first scale, the second parameter of the model which is the weight allocated to each property in the objective function was also included in a feedback loop.

### Tuning of the weights

The weights allocated to each property can be tuned to reach a better result, the weight tuning scale is defined by:

$$S_w = \frac{\log(w)}{\log(W)} \quad (27)$$

$W$  is the maximal weight over the whole studied sets of weights and  $w$  is the maximal weight of the studied set of weights.  $W$  is given by the stopping criterion, achieved when the objective function based on the fraction values,  $O_g$ , did not decrease more than 1% during three consecutive iterations. This criterion could be strengthened to enhance the accuracy but 1% enabled a good result to be reached within an acceptable computing time. An iteration corresponds to an increase of the maximal weight value  $10^M$  by a factor 10.

The accuracy of the model depending on the weight tuning scale is discussed only for a reduced number of molecule tuning scales. To analyze the effect of improving 0, 1, 2, 3, or 4 hydrocarbon groups,  $S_m$  was set equal to 0, 0.22, 0.44, 0.55 and 1 (see Table 8).

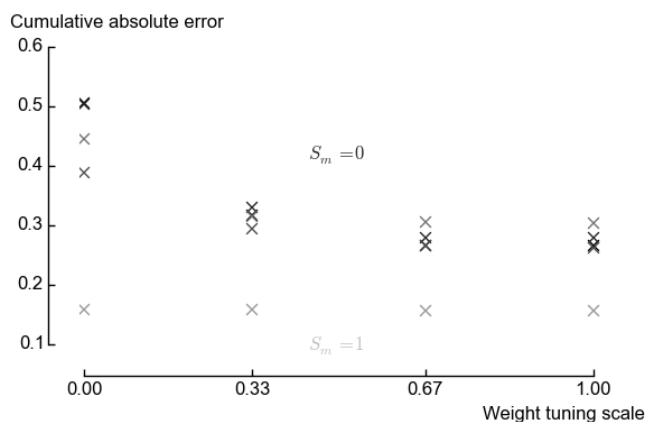


Figure 4. Absolute cumulative error along the weight refinement at a molecule tuning scale equal to 0, 0.22, 0.44, 0.55 and 1 (from darker to lighter grey).

The stopping criteria was respected for all the molecule tuning scales when the maximal weight was set at  $1.10^3$ . The cumulative absolute error without considering the confidence interval is reduced under this condition for all the molecule databases (Figure 4). The error plunges when the maximal weight value evolves from 1 to 10, thus, relying on a maximal weight of 10 could be appropriate. The weights do not have a significant impact when the best molecule tuning scale is considered and the error cannot be reduced less than approximately 30% with the other molecule tuning scales. According to the present study, weights are not needed at a molecule tuning scale of 1 because the error and the compositions are constant along the weight tuning scale (Table 10).

Table 10. Calculated fractions (% wt/wt) and cumulated absolute error from confidence interval comparison ( $\epsilon_{CI}$ , %) at a molecule tuning scale equal to 1, and at a weight tuning scale equal to 0, 0.33, 0.67 and 1.

$S_w$	P	I	O	N	A	Ox	$\epsilon_{CI}$ (%)
0	0.3	11.2	30.1	13.4	32.1	12.8	12.6
0.33	0.0	11.2	30.4	13.5	32.0	12.8	12.7
0.67	0.0	11.4	30.0	13.7	32.0	12.9	12.4
1	0.0	11.4	30.0	13.7	32.0	12.9	12.4

The range of validity of the model according to the fuel variability is not yet studied but it will probably decrease if the weight tuning scale is too high and especially fitted for the reference fuel. The ability to reduce the error with a good set of weights (Figure 4) could be used to obtain better results when a deviation of the fuel composition is observed.

The developed methodology enabled a good accuracy. However, the range of applicability of the method probably decreases when the inputs are tuned to reach a high accuracy. Therefore, comparing the error propagation of a variation of the fuel composition on the calculated fraction is an interesting approach to complete the current results and find an optimum set of parameters (molecule database and weights) to couple a good range of applicability with a good accuracy. Then, the key parameter between the molecule tuning, the weight tuning, or a combination of both, for achieving good results for a wide range of composition will be determined.

## Conclusion

In this paper, the existing models for predicting the composition of a classical fuel are extended to a model suited for unconventional fuels. As an example, a model for automotive shredder residues (ASR)-derived gasoline-like fuels was used as case study. The method relies on the chemical analysis of a reference fuel which characterizes well the unconventional fuel. Once the model is set according to this reference fuel, the chemical analysis is not required anymore and the fuel properties measured according to standard test methods are sufficient. Thereafter, the approximated fuel fractions can be used for several purposes. First, the octane numbers can be estimated thanks to the pseudo-component technique which is relevant as unconventional fuels are often related to constraints (cost, reliability) and are in general produced locally making it hard to perform the same kind of quality control as in a large plan like cooperative fuel research (CFR) tests. Secondly, the unconventional fuel production can be monitored. Lastly, a variation of the fuel characteristics can be explained. Therefore, the developed methodology enables the properties of an unconventional fuel to be studied during its production, allowing to get retrofitting information, to make technical

choices, to study the production stability or to tune the process towards better combustion.

Compared to the existing methods, where a linear system of equations based on two fuel properties is solved to calculate the paraffin, naphthene, aromatic (PNA) fractions, this method uses the pseudo-component technique and six properties simultaneously, namely the refractive index (n), the viscosity gravity function (VGF), the Watson K-factor ( $K_w$ ), the specific gravity (SG), the stoichiometric air-to-fuel ratio (AF<sub>s</sub>), and the oxygen content, leading to solve an optimization problem rather than a direct linear system of equation. This method significantly extends the existing methods to less traditional fuels and enables a good estimation of the n-paraffin, iso-paraffin, olefin, naphthene, aromatic, oxygenate (PIONAOx) fuel fractions. The six properties can be easily measured thanks to ASTM standards. The accuracy depends on the parameters of the model and is evaluated comparing the calculated fractions to the confidence intervals of the real fractions estimated from the composition measured with the comprehensive two-dimensional gas chromatography (GC × GC). The error is low when the model is well-set. For the best estimated composition, the cumulated error of all the groups was evaluated at 12.4%.

Further studies must investigate the range of applicability of the current methodology. Tuning the parameters of the model based on one given reference fuel composition could probably decrease the range of applicability. Therefore, studying the link between the accuracy and the range of applicability for different parameters will bring an additional major information. The accuracy could be further enhanced because oxygenate molecules overlap even with a comprehensive two-dimensional gas chromatography technique. The oxygenate fraction was estimated from the atomic oxygen content and this method could be improved.

## References

1. InnovaTech. "Projet Phoenix - Une magnifique vitrine technologique pour la Wallonie," <http://clusters.wallonie.be/servlet/Repository/dossier-de-presse-comet-traitements.pdf?ID=43889&saveFile=>, November 2013.
2. Cossu, R. and Lai, T., "Automotive shredder residue (ASR) management: An overview," *Waste Management*, 45:143-151, 2015, doi:10.1016/j.wasman.2015.07.042.
3. European commission, "Directive 2000/53/EC of the European parliament and of the council on end-of-life vehicles," <http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32005L0064>, 2005.
4. European Union website, "End-of-life vehicle statistics," [http://ec.europa.eu/eurostat/statistics-explained/index.php/End-of-life\\_vehicle\\_statistics](http://ec.europa.eu/eurostat/statistics-explained/index.php/End-of-life_vehicle_statistics), October 2016.
5. Riazi, M.R., "Characterization and Properties of Petroleum Fractions," 2005, doi:10.1017/CBO9781107415324.004.
6. Jody, B.J., Daniels, E.J., Duranceau, C.M., Pomykala, J.A. et al., "End-of-Life Vehicle Recycling: The State of the Art of Resource Recovery from Shredder Residue," *Waste Management*, 45:143-151, 2015, doi:10.2172/925337.
7. Ayanoglu, A and Yumruş, R., "Production of gasoline and diesel like fuels from waste tire oil by using catalytic pyrolysis," *Abdulkadir Energy*, 103:456-468, 2016, doi:10.1016/j.energ.2016.02.155.
8. ASTM International, "Standard Test Method for Research Octane Number of Spark-Ignition Engine Fuel," ASTM D2699-15a, 2015, doi:10.1520/D2699-15A.
9. ASTM International, "Standard Test Method for Detailed Analysis of Petroleum Naphthas through n-Nonane by Capillary Gas Chromatography," ASTM D5134-13, 2013, doi:10.1520/D5134.
10. ASTM International, "Standard Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100-Metre Capillary High Resolution Gas Chromatography," ASTM D6729-14, 2014, doi:10.1520/D6729-14.
11. ASTM International, "Standard Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100Metre Capillary (with Precolumn) High-Resolution Gas Chromatography," ASTM D6730-01(2016), 2016, doi:10.1520/D6730-01R16.
12. ASTM International, "Standard Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 50-Metre Capillary High Resolution Gas Chromatography," ASTM D6733-01(2016), 2016, doi:10.1520/D6733-01R16.
13. ASTM International, "Standard Test Method for Hydrocarbon Types, Oxygenated Compounds, and Benzene in Spark Ignition Engine Fuels by Gas Chromatography," ASTM D6839-16, 2016, doi:10.1520/D6839-17.
14. Flood, M.E., Connolly, M.P., Comiskey, M.C. and Hupp, A.P., "Evaluation of single and multi-feedstock biodiesel - diesel blends using GCMS and chemometric methods," *Fuel*, 186:58-67, 2016, doi:10.1016/j.fuel.2016.08.069.
15. Widgren, J.A. and Bruno, T.J., "Thermal Decomposition Kinetics of the Aviation Turbine Fuel Jet A," *Ind. Eng. Chem. Res.*, 47:4342-4348, 2008, doi:10.1021/ie8000666.
16. Yu, J., Ju, Y., and Gou, X., "Surrogate fuel formulation for oxygenated and hydrocarbon fuels by using the molecular structures and functional groups," *Fuel*, 166:211-218, 2015, doi:10.1016/j.fuel.2015.10.085.
17. Liu, Z. and Phillips, J.B., "Comprehensive Two-Dimensional Gas Chromatography using an On-Column Thermal Modulator Interface," *Journal of Chromatographic Science*, 29:227-231, 1991, doi:10.1093/chromsci/29.6.227.
18. Zeng, H., Zou, F., Lehne, E., Zuo, J.Y., et al., "Advanced Gas Chromatography-Progress in Agricultural, Biomedical and Industrial Applications," (InTech, 2012), 363-388, doi:10.5772/2518.
19. Dijkmans, T., Djokic, M.R., Van Geem, K.M. and Marin, G.B., "Comprehensive compositional analysis of sulfur and nitrogen containing compounds in shale oil using GC × GC FID/SCD/NCD/TOF-MS," *Fuel*, 140:398-406, 2015, doi:10.1016/j.fuel.2014.09.055.
20. Adam, F., Bertoini, F., Coupard, V., Charon, N. et al., "Using comprehensive two-dimensional gas chromatography for the analysis of oxygenates in middle distillates. I. Determination of the nature of biodiesels blend in diesel fuel," *Journal of Chromatography A*, 1186(1-2):236-244, 2008, doi:10.1016/j.chroma.2007.12.063.
21. Alborzi, E., Blakey, S., Ghadbeigi, H., Pinna, C. et al., "Investigation of surface deposition in a simulated fuel injector feed arm with sudden expansion/contraction," *Fuel*, 186:534-543, 2016, doi:10.1016/j.fuel.2016.08.080.
22. Rockstroh, T., Floweday, G., and Yates, A., "Optimisation of synthetic gasoline blend recipes for use in modern charge boosted GDI engines," *Fuel*, 186:800-820, 2016, doi:10.1016/j.fuel.2016.09.001.
23. Wang, F.C.-Y., Qian, K., and Green, L.A., "GC × MS of diesel: A two-dimensional separation approach," *Analytical Chemistry*, 77(9):2777-2785, 2005, doi:10.1021/ac0401624.
24. ASTM International, "Organic Analysis of Distillate by Comprehensive Two-Dimensional Gas Chromatography with Flame Ionization Detection," UOP990-11, 2011.

25. Jennerwein, M.K., Sutherland, A.C., Eschner, M., Gröger, T. et al., "Quantitative analysis of modern fuels derived from middle distillates - The impact of diverse compositions on standard methods evaluated by offline hyphenation of HPLC-refractive index detection with GC × GC-TOFMS," *Fuel*, 187:16-25, 2017, doi:10.1016/j.fuel.2016.09.033.
26. Ristic, N.D., Djokic, M.R., Konist, Van Geem, K.M., et al., "Quantitative compositional analysis of Estonian shale oil using comprehensive two dimensional gas chromatography," *Fuel Processing Technology*, 167:241-249, 2017, doi:10.1016/j.fuproc.2017.07.008
27. Inficon, "Response Factors for Flame Ionization Detector Operation," <http://www.raeco.com/products/gasmonitoring/Photovac-Inficon-MicroFID-II/FID-response-factors-diaf56a1-2012.pdf>, 2012.
28. Schofield, K., "The enigmatic mechanism of the flame ionization detector: its overlooked implications for fossil fuel combustion modeling," *Progress in Energy and Combustion Science*, 34:330-350, 2008, doi:10.1016/j.pecs.2007.08.001.
29. Hoff, A., Jacobsson, S., Pfaffli, P., Zitting, A. et al., "Degradation products of plastics. Polyethylene and styrene-containing thermoplastics-analytical, occupational and toxicologic aspects," *Scand J Work Environ Health*, 8(2):1-60, 1982, doi:10.1080/02844310310023909.
30. Sarker, M., Rashid, M.M, Molla, M. and Rahman, M.S, "Thermal Conversion of Waste Plastics (HDPE, PP and PS) to Produce Mixture of Hydrocarbons," *American Journal of Environmental Engineering*, 2(5):128-136, 2012, doi:10.5923/j.ajee.20120205.03.
31. Ahmed, T.H., "Hydrocarbon Phase Behavior," (Gulf Publishing Company, 1989), ISBN:0-87201-589-0.
32. ASTM International, "Standard Test Method for Distillation of Petroleum Products and Liquid Fuels at Atmospheric Pressure," ASTM D86-17, 2017, doi:10.1520/D0086-17.
33. Aspen Technology, Inc., "Aspen Physical Property System. Physical Property Methods V8.4," 2013.

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## Definitions/Abbreviations

<b>v<sub>38</sub></b>	Kinematic viscosity at 38°C
<b>ABS</b>	Acrylonitrile butadiene styrene
<b>AC<sub>w</sub></b>	Atom A to carbon weight ratio
<b>AF<sub>s</sub></b>	Air-to-fuel ratio under stoichiometric conditions
<b>API</b>	American Petroleum Institute
<b>ASR</b>	Automotive shredder residues
<b>CFR</b>	Cooperative fuel research

<b>DLF</b>	Diesel-like fuel
<b>EA</b>	Elemental analyzer
<b>ELV</b>	End-of-life cars
<b>EPDM</b>	Ethylene propylene diene monomer
<b>FID</b>	Flame ionization detector
<b>GC</b>	Gas chromatography
<b>GC-MS</b>	Gas chromatography mass spectrometry
<b>GLF</b>	Gasoline-like fuel
<b>GC × GC</b>	Comprehensive two-dimensional gas chromatography
<b>HC</b>	Hydrogen-to-carbon mass fraction
<b>I</b>	Refractive index parameter
<b>K<sub>w</sub></b>	Watson K factor
<b>m</b>	m-parameter
<b>MeABP</b>	Mean average boiling point
<b>Mm</b>	Molar mass
<b>n<sub>20</sub></b>	Refractive index at 20°C
<b>NCD</b>	Nitrogen chemiluminescence detector
<b>OC</b>	Oxygen-to-carbon mass fraction
<b>PA</b>	Polyamide
<b>PIONAOx</b>	n-paraffin, iso-paraffin, olefin, naphthene, aromatic, oxygenate
<b>PNA</b>	Paraffin, naphthene, aromatic
<b>PP</b>	Polypropylene
<b>PS</b>	Polystyrene
<b>PUR</b>	Polyurethane
<b>RF</b>	Response factor
<b>PVC</b>	Polyvinyl chloride
<b>R<sub>i</sub></b>	Refractivity intercept
<b>RON</b>	Research octane number

<b>SCD</b>	Sulfur chemiluminescence detector
<b>SG</b>	Specific gravity
<b>SL</b>	10-90 slope
<b>S<sub>m</sub></b>	Molecular tuning scale
<b>S<sub>w</sub></b>	Weight tuning scale
<b>T<sub>b</sub></b>	Normal boiling point
<b>TOF</b>	Time of flight
<b>VABP</b>	Volume average boiling point
<b>VGf</b>	Viscosity gravity function
<b>ω</b>	Moles of oxygen under stoichiometric condition