

1 Understanding the compositional effects of SAFs on combustion intermediates

2 M. Mehl^{1*}, M. Pelucchi¹, P. Osswald²

3 ¹ CRECK Modeling Lab, Department of Chemistry, Materials and Chemical Engineering “G. Natta”,
4 Politecnico di Milano, P.zza Leonardo da Vinci 32, 20133 Milano, Italy

5 ² German Aerospace Center (DLR), Institute of Combustion Technology, Pfaffenwaldring 38-40,
6 70569 Stuttgart, Germany

7 ***Correspondence:**

8 Corresponding Author

9 marco.mehl@polimi.it

10 **Keywords: Chemical kinetics, flow reactor, renewable fuels, combustion modeling, surrogates**

11 Abstract

12 This work analyses, experimentally and numerically, the combustion behavior of three aviation fuels:
13 a standard Jet A-1, a high aromatic content fuel, and an isoparaffinic Alcohol to Jet (ATJ) fuel. The
14 goal is to demonstrate the ability of a chemical kinetic model to capture the chemistry underlying the
15 combustion behavior of a wide range of jet fuels, starting from compositional information. Real fuels
16 containing up to hundreds of components are modeled as surrogates containing less than 10
17 components, which represent the chemical functionalities of the real fuel. By using an in-house
18 numerical optimizer, the fuel components and their relative quantities are selected, and a semi-detailed
19 kinetic model (containing about 450 species) is used to simulate the formation of the main oxidation
20 products and reaction intermediates. Calculations are compared with species profiles measured in a
21 laminar flow reactor to validate the model and provide insights into the reactivity of the fuels. Finally,
22 starting from the results, general observations on the strengths and limits of the approach are provided,
23 highlighting areas where further investigations are required.

24 1 Introduction

25 Hard-to-decarbonize sectors, such as aviation, require mid- to long-term solutions to meet climate
26 change mitigation targets. According to the recent reports emerging from the 2050 Waypoint project
27 [1], an Air Transport Action Group initiative, the greatest opportunity for decarbonizing the aviation
28 sector comes from an aggressive transition to sustainable aviation fuels (SAFs): Hydroprocessed Esters
29 and Fatty Acids (HEFA), Fisher Tropsch, Alcohol to Jet (ATJ), and Power to Liquid (PtL) fuels. The
30 diversity of resources from which SAFs can be produced, will unavoidably expand the chemical
31 complexity of future fuels.

32 For this reason, programs such as JETSCREEN [2] have been supported by the EU to effectively tackle
33 the critical process of fuel optimization, qualification and approval. The final goal is to provide tools
34 that, by means of experimental tests and accurate models, will be capable of assessing a priori the
35 compatibility of new SAFs (and mixtures of SAFs and traditional fuels) with existing infrastructures
36 (i.e. engines, fuel system). In this framework, a key step is the capability of correctly predicting relevant

Compositional effects of SAFs

37 combustion properties such as auto-ignition propensity, laminar flame speed and pollutants emissions
38 (e.g., soot) starting from compositional information. The development of detailed chemical kinetic
39 models serves the goal of predicting fuel behavior ahead of possible experimental campaigns for any
40 new candidate fuel or fuel component that might be of interest in the area of SAFs.

41 Specifically, when a novel fuel mixture emerges, simpler multicomponent fuel surrogates are
42 developed by means of optimization algorithms that take into account compositional data (e.g., GCxGC
43 data) and other target properties such as viscosity, density, distillation curve, heat of combustion, H/C
44 ratio, smoke point, *etc.* In the context of kinetic modeling, such surrogates are typically composed of
45 3 to 10 compounds, which, mixed together, allow to match the properties of the fuel under
46 investigation. For each of these components a dedicated kinetic subset (i.e., a network of elementary
47 chemical reactions) is developed to model its combustion properties (e.g., ignition delay times, laminar
48 flame speed, intermediate and by-products formation). Such models are validated by means of
49 comparisons with experimental data available in literature for pure components and their blends in 0-
50 D or 1-D laminar reactors and flames, where the chemical kinetic effects are entirely, or at least
51 significantly, decoupled from heat and mass transfer phenomena. Validated kinetic models can then be
52 used to perform targeted parametric analysis to unravel temperature, pressure and composition
53 dependency of the combustion characteristics in such simple systems. Furthermore, skeletal model
54 reduction can be used to bring down the size of such models, making them applicable to large scale (2-
55 D or 3-D) fluid dynamic simulation of real, or close-to-real, systems. This approach can speed up the
56 fuel screening process and support the optimization of combustion devices, favoring the full market
57 implementation of SAFs. Indeed, even by exercising the model on simple systems, it is possible to
58 draw relevant conclusions about the ignitability of mixtures, their burning velocities, their soot
59 propensity and blending behavior.

60 On these premises, this work analyzes, experimentally and numerically, the combustion behavior of
61 three aviation fuels: a standard Jet A-1 (A1), an isoparaffinic Alcohol to Jet fuel (B1), and a high
62 aromatic fuel (C1). The standard jet fuel, formulated in a previous study [3], is used as a reference,
63 while the renewable ATJ fuel (derived from iso-butanol) and the high aromatic content fuel, present
64 extreme compositional features: the ATJ is almost entirely constituted by a single highly-branched iso-
65 alkane, while the high aromatic fuel contains unusually high fractions of mono- and di-aromatics.
66 Compositional information and global composition indexes such as H/C ratio and average molecular
67 weight for the three fuels are reported in Table 1.

68 While other literature works discuss the development and validation of fuel surrogates and models for
69 specific fuels[4]–[7], this paper focuses on the methodological aspects involved in the definition of
70 general models aiming at capturing fundamental aspects of the fuel chemistry. In this work, combustion
71 chemistry models for three highly diverse fuels are obtained by coupling a single comprehensive
72 kinetic mechanism and a surrogate formulation approach incorporating compositional information. The
73 fuel models are then validated against well-characterized kinetic data from the DLR flow reactor. The
74 final goal is to demonstrate how the workflow here presented allows capturing the speciation profiles
75 of a broad range of fuels with high accuracy and enables the analysis of the relative behavior of the
76 fuels on a more fundamental level. The rationale is that reaction intermediates are strictly related to the

Compositional effects of SAFs

77 composition of the active radical pool that controls fuel oxidation and ultimately determines global
78 combustion characteristics such as auto-ignition, flame behavior and soot formation. This successful
79 validation, therefore, represents an important step towards predictive models for new candidate fuels
80 able to predict features of practical interest such as burning velocity, emissions [3], [8], high altitude
81 relight [9], and lean blow off [10], [11].

82 **2 Predictive models for SAFs: Methods**

83 **2.1 Experimental facility and procedures**

84 The first step towards the development of validated models for the combustion of jet fuels is the
85 experimental evaluation of their oxidative behavior in well-characterized conditions. To achieve this
86 goal, species profiles for selected fuels have been measured by DLR in a high-temperature flow reactor
87 coupled to a molecular beam mass (MBMS) spectrometer. This set up allows for in-depth investigation
88 of relevant combustion chemistry features by identifying simultaneously multiple intermediates and,
89 therefore, reaction channels controlling the formation of products [12]. The species profiles measured
90 provide useful validation data for the development of detailed chemical kinetic model, enabling the
91 assessment of the impact of fuel composition on emissions in technical combustors. Figure 1 provides
92 an overview of the experimental apparatus. Since a comprehensive literature was recently produced on
93 this specific experimental setup [13]–[15], only a brief description is given here.

94 The system can be divided into two segments: a high-temperature laminar flow reactor including gas
95 supply and a vaporizer system, and a molecular beam mass spectrometry (MBMS) time-of-flight
96 detection (TOF) system. The reactor exit is positioned to the sampling nozzle of the MBMS-TOF
97 system and gas is sampled directly from the reactor outlet and transferred to the high-vacuum detection
98 system.

99 The reactor features a ceramic tube (total length of 1497 mm); a laminar flow of highly diluted (> 99%
100 Ar) mixture is fed into the reactor. The high dilution suppresses significant volumetric heat release
101 allowing a better control on the temperature profile in the reactor. A relatively large inner diameter (40
102 mm) allows minimizing boundary effects. A commercial setup (Bronkhorst, CEM) is used in the
103 mixture preparation section to vaporize the fuel. All input streams are metered in high precision
104 (accuracy ± 0.5 %) by Coriolis mass flow meters. The high dilution of the system also guarantees the
105 complete evaporation of the fuels, whose partial pressures are maintained below 100 Pa.

106 Operating conditions are designed to yield constant carbon flow at slightly rich ($\Phi = 1.2$) and lean (Φ
107 = 0.8) conditions, respectively. Oxygen concentration is adjusted according to the desired
108 stoichiometry. The exact stoichiometry was determined by measuring the hydrogen content of the fuels
109 using low resolution pulsed NMR (ASTM D7171). The heteroatoms content is assumed to be
110 negligible. The obtained H-content is summarized in Table 2 with the respective inlet flow conditions.

111 Homogeneous flow conditions are obtained by feeding the premixed gases through a tempered flange
112 equipped with a porous bronze plug. The reaction segment is 1000 mm long, and is contained in
113 customized high-temperature oven (Gero, Type HTRH 40-1000), capable of reaching temperatures up

Compositional effects of SAFs

114 to 1900 K. Samples taken at the reactor exit are transferred to high vacuum (10^{-6} mbar) by a two-stage
115 differential pumping system. The rapid expansion quenches chemical reactions immediately by
116 lowering temperatures and concentrations, effectively “freezing” the composition. Detection is carried
117 out using an electron impact (EI) time-of-flight (TOF) mass spectrometer (Kaesdorf, mass resolution
118 $R = 3000$). This system is able to determine the elemental composition of combustion intermediates
119 within a C/H/O system. Soft electron energies are applied (10.6eV) to avoid species fragmentation
120 during the ionization process. Additionally, a quadrupole mass spectrometer is positioned in the
121 ionization chamber (off beam) and operated at a higher electron energy (70 eV) to track major species
122 contemporarily to the MBMS-TOF measurements. Details on the experimental setup, including a
123 schematic and its instrumentation, may be found in previous publications [12], [13].

124 A monotonically decreasing temperature ramp (-200 K/h) is applied to the oven and all measurements
125 are performed maintaining a constant inlet mass flow. A temperature window spanning from 600 K to
126 1200 K was scanned, covering all regimes between the absence of reactions to full conversion and
127 thermal equilibrium. The flow regime is laminar for all the temperature conditions, but previous studies
128 demonstrated how this system can be successfully simulated treating the system as one-dimensional,
129 adopting a predefined axial temperature profile derived from the experiments and the plug flow
130 hypothesis for kinetic calculations [12], [16]. Temperature profiles along the reactor axis were
131 measured during the temperature ramps, providing the necessary boundary condition for the kinetic
132 model.

133 The quantitative evaluation of the species was performed adopting well established techniques [12],
134 [17], [18] performing direct binary (species/Ar) calibration measurements or estimating the ionization
135 cross section based on the RICS (Relative Ionization Cross Section) method. Calibration by direct cold
136 gas measurements was performed for most species. The estimation procedure (RICS) was applied for
137 all radicals, as well as for C_2H_2O , C_7H_8 , C_8H_6 , C_8H_8 , C_9H_8 , $C_{12}H_8$, $C_{12}H_{10}$, $C_{13}H_{10}$, and $C_{14}H_{10}$. Note
138 that species predominantly showing a fuel-like behavior (i.e., maximum concentration at low
139 temperature) are calibrated internally using the respective fuel composition determined by two
140 dimensional gas chromatography (GCxGC) obtained by IFPEN.

141 For the three fuels, more than 500 quantitative species profiles could be obtained at two equivalence
142 ratio conditions. Results are obtained as a function of the oven temperature. Further details about the
143 experimental set-up and additional data are available in [19]. Figure 2 summarizes the major species
144 (product and reactants) for all initial compositions.

145 A similar global reaction behavior was observed for all fuels with moderate temperature shifts across
146 the fuels. The highly-branched paraffinic ATJ (B1) fuel is shifted to slightly higher temperatures,
147 indicating a longer total ignition delay time. Figure 3 summarizes some selected soot precursor
148 intermediate species: benzene C_6H_6 , indene C_9H_8 , naphthalene $C_{10}H_8$, and anthracene $C_{14}H_{10}$. Note that
149 naphthalene is also contained in the real fuel, therefore starting with a non-zero concentration. For
150 these species a clear correlation with the fuel composition can be drawn. As can be expected, soot
151 precursor species are more abundant in fuels with higher aromatic content (or low hydrogen content).

Compositional effects of SAFs

152 Hydrogen content is considered to be a useful indicator for sooting propensity at technical combustors'
153 conditions such as jet engines [20].

154 **2.2 Kinetic modeling of real fuels**

155 Describing the chemistry controlling the combustion of a real fuel in terms of its fundamental kinetic
156 processes is a daunting task: typically, real fuels are mixtures of hundreds of components whose exact
157 chemical structure is often unknown. Moreover, the full combustion of each fuel component is the
158 result of tens, hundreds, if not thousands of elementary reactions whose rate needs to be determined.
159 Finally, suitable solvers are needed to effectively compute the ODE (Ordinary Differential Equation)
160 and DAE (Differential Algebraic Equation) systems describing the chemical evolution of the system.
161 The following sections detail the approaches and the different steps used to obtain an accurate and
162 predictive model able to represent the chemistry involved in the combustion of jet fuels of practical
163 interest.

164 **2.2.1 The kinetic model**

165 Detailed kinetic models attempt to identify all the important reaction pathways controlling the
166 combustion of fuel components, and to assign to each elementary step temperature and pressure
167 dependent reaction rates (i.e., the larger is the molecule, the higher is the number of reactions involved
168 in its oxidation). Thermodynamic properties are used to define rate constants of backward reactions
169 for reversible elementary steps. The two main challenges a kinetic model has to address are: i) the
170 identification of the relevant reaction intermediates (whose number dictates the number of equations
171 required to calculate the composition of the system), and ii) the determination of the thousands of
172 reaction rate parameters it includes, together with thermodynamic properties of each species.

173 Because of the complexity of detailed kinetic models and of the computational burden associated with
174 their use, reduced models including a smaller number of intermediates and global reactions are
175 generally preferred for practical calculations and combustors' design. The model proposed by the
176 CRECK Modelling Lab of Politecnico di Milano attempts to couple the fundamentals of detailed
177 chemical kinetic models and the practicality of reduced models, by limiting the number of species (and
178 therefore of reactions) through isomer lumping [21].

179 By doing so, it is possible to simulate the fundamental processes controlling combustion and by-
180 products formation of complex mixtures of large molecules with a relatively low number of species
181 (few 100s), reducing considerably the computational cost of simulations and easing the interpretation
182 of relevant chemical pathways. The CRECK model (which is meant to be general and applicable to a
183 wide window of operating conditions) can be further reduced for computational fluid-dynamic
184 applications based on the specific windows of compositions and thermodynamic conditions of interest
185 (e.g., T , p , φ).

186 The other main challenge is the determination of reaction rates. While an extensive *corpus* of
187 experimental and fundamental work exists on the reaction rates of small hydrocarbons (1-2 carbon
188 atoms), most of the reactions involved in the oxidation of heavier molecules cannot be easily measured
189 or calculated using quantum-chemical approaches. To overcome this issue, a systematic approach

Compositional effects of SAFs

190 based on modularity, hierarchy and self-consistency is used in the construction of models for large fuel
191 molecules.

192 The model is built hierarchically from light to heavy fuel species starting from a reaction mechanism
193 core which describes the oxidation and pyrolysis of small gas-phase hydrocarbons. The current version
194 of the CRECK model [22] adopts the Aramco 2.0 [23], [24] as its core. The core, which includes
195 species up to 3 carbon atoms in size (C3), provides the basis for additional modules including larger
196 molecules ([25], [26]). At high temperature, the first step in the oxidation of large hydrocarbons is their
197 decomposition to smaller fragments. Reactions involving C3 hydrocarbons or lower are subsets of the
198 oxidation mechanisms of larger species which form them by fragmentation. By expanding the model
199 towards heavier fuels, it is possible to describe the oxidation of larger molecules through the addition
200 of blocks of reactions, which are built and validated starting from the core and moving up. Jet fuels
201 include components with a number of carbons in the C7-C16 range and their kinetic models require
202 the determination of a large number of parameters to quantify the reaction rates involved. From a
203 micro-kinetic standpoint, the primary oxidation steps controlling combustion show strong similarities
204 within a certain family of fuel components (paraffins, olefins, aromatics, naphthenes, etc.). For this
205 reason, using analogy rules, it is possible to estimate reaction rates for molecules that have not been
206 studied before. Adhering to principles of hierarchy, modularity, and self-consistency among reaction
207 classes built on structural similarities, the CRECK team developed models for many components
208 relevant to mid-distillates' combustion. Among these, based on the compositional analysis provided
209 by IFPEN, a set of components representative of the ones detected in the real fuels were selected (e.g.,
210 C12 n- and iso-alkanes, decalin, butylbenzene, butylcyclohexane, etc.).

211 The CRECK kinetic model covers both high ($T > 1000\text{K}$) and low temperature ($T = 500\text{-}1000\text{K}$)
212 reactions. High-temperature reactions are relevant to flame conditions and pollutant formation, while
213 the low-temperature reactions ($600\text{-}900\text{K}$) are required to predict the auto-ignition propensity of the
214 fuel. At high pressure, low-temperature reactions become more important and they should be included
215 in a comprehensive model to guarantee accurate predictions, particularly when transients are simulated.

216 Thermodynamic properties for all the species in the model have been adopted from the active
217 thermochemical tables [27], from the online repository compiled by Burcat [28], or determined based
218 on group additivity methods. The final kinetic model includes about 460 species and 14000 reactions,
219 although, depending on the components and the operating window of interest, it is possible to reduce
220 the size of the model for specific applications by removing non-relevant kinetic modules.

221 **2.2.2 Surrogate formulation**

222 While the detailed composition of a full-blend fuel is rarely fully resolved, simpler analytical
223 techniques allow to determine the breakdown into families of compounds, or their H/C ratio. Two
224 dimensional gas chromatography (GCxGC) allows for a much more refined analysis, detecting both
225 the family and the molecular weight distribution of the components.

226 Because of compositional complexity and lack of accurate information, it is not feasible to simulate
227 the chemical behavior of a fuel reproducing its exact composition, especially when a detailed kinetic
228 modelling approach is sought. In this case, modelers often adopt the surrogate approach: a simpler

Compositional effects of SAFs

229 mixture (<10 components) matching a set of target properties of the real fuel is selected and used to
230 represent the real fuel [4]–[6]. The selection of the surrogate can be performed “manually” by an expert
231 user or, especially when many targets and fuel components are to be included, using an optimization
232 tool.

233 In this work a hybrid approach has been selected, where the fuel palette used in the optimization is
234 “manually” selected and, following the numerical optimization, minor variations are introduced to
235 account for finer details relevant to the fuel composition (e.g., small amounts of a specific family of
236 components that can play a role in the pollutant formation processes).

237 The first step in surrogate formulation is the definition of the palette of components to be included in
238 the optimization. Since our goal is to generate a kinetic model for jet fuels, it is important to choose
239 fuel components for which a reliable kinetic model exists (or can be easily built) and, ideally, has
240 already been extensively validated. Figure 4 shows the set of components currently adopted for the
241 fuel surrogate palette.

242 In the context of this project, POLIMI developed a fuel surrogate optimization tool. The optimization
243 of the composition of a fuel surrogate is a multi-target multidimensional problem. The number of
244 targets to be matched can be in the order of the 10s, while the dimensionality is equal to the number of
245 components included in the palette minus one, with multiple solutions. Different optimization
246 strategies have been proposed in literature for this type of problems (machine learning and genetic
247 algorithms are among them) [29], [30]. The optimizer used in this work exploits the optimization
248 package available in Matlab and is inspired by a previous literature work by Narayanaswamy et al.
249 [31]. Different optimization algorithms are available within the tool developed at CRECK, including
250 local optimization and a genetic algorithm.

251 The optimization targets available at this stage are DCN, H/C ratio, distribution within the different
252 family of components, average molecular weight, threshold sooting index, density, distillation curve,
253 and liquid viscosity. More targets will be added in future works to accommodate all the properties
254 deemed important for the scopes of SAFs design, optimization and approval.

255 Based on this optimization process, surrogates were formulated for fuels A1 and C1. Fuel B1 is a
256 synthetic fuel with a well-defined composition: the GCxGC data provided by IFPEN clearly identified
257 iso-alkanes as the only components and, based on the process involved in its production and the
258 compositional information available, it is possible to infer that these iso-alkanes are strongly branched
259 oligomers of iso-C4 units. The GCxGC indicates that a C12 iso-paraffin is the main component and a
260 surrogate based on iso-dodecane and iso-cetane was selected accordingly. Table 3 summarizes the
261 composition of the three surrogates.

262 Figure 5 compares the distillation curves measured for the three jet fuels using the ASTM D86 standard
263 method against the distillation curve calculated for the surrogates using a standard equilibrium
264 approach for ideal mixtures (i.e., a linear combination of partial pressures calculated using the Antoine
265 coefficients from [32]). The distillation curve calculated for the surrogate of fuel A1 matches with good
266 approximation the experimental one targeted in the surrogate optimization process. Similarly, the
267 calculated distillation curve for the surrogate of fuel B1, which was formulated directly from the
268 compositional information provided by IFPEN, agrees very well with the measurements. The

Compositional effects of SAFs

269 distillation curve for fuel C1, as anticipated, shows greater deviations. Because of the lack of fuel
270 components suitable to reproduce both the distillation curve and the H/C ratio, priority was given to
271 the H/C ratio, a fundamental chemical property. Future works will add new components to the
272 surrogate palette to overcome the current limitation. In particular, based on the GCxGC analysis, the
273 need for higher molecular weight alkyl-cycloparaffins emerged. The surrogate for fuel C1, still, results
274 to be the least volatile among the three fuels, reproducing, at least qualitatively, the relative behavior
275 of the fuels.

276 3 Results

277 The flow reactor data collected at DLR have been simulated using OpenSmoke++ [33]. Calculations
278 allowed to estimate the gas composition at the exit of the reactor for temperatures between 800 and
279 1150K (nominal temperature) at two equivalence ratios ($\varphi=0.8$ and 1.2). Not all the measured species
280 can be directly compared with the experiments, as the surrogates mimic the composition of the real
281 fuel by targeting the moieties it contains, and not the actual fuel component concentrations. A clear
282 example comes from naphthalene, which can be both a secondary product formed during combustion
283 and a fuel component. For this reason, in the following comparisons, we focus mostly on the smaller
284 species that are formed during the decomposition and oxidation of the initial fuel and that may have an
285 impact on the following soot and NO_x formation processes. However, because of the relevance of
286 polycyclic species to the formation of PAHs, naphthalene concentration profiles are shown for all the
287 fuels.

288 3.1 Fuel A1 (JET A-1)

289 Figures 6 and 7 show the comparisons between calculations and experiments for Jet fuel A-1 (i.e., the
290 standard jet fuel). The fuel model (constituted by the combination of the surrogate and the relative
291 kinetic model) correctly reproduces the profiles of the major products, the consumption of the oxidizer
292 (O₂) and the formation of the final combustion products. H₂O and CO₂ are well captured, while small
293 discrepancies are observed for H₂ and CO. The peak in H₂ concentration is measured at about 1020 K;
294 the model accurately predicts its rate of formation, but has a slight delay in the onset of its consumption.
295 The CO peak is reproduced correctly, although its shape is somewhat sharper. This could be partially
296 related to the simplified approach adopted in the simulation of the flow reactor, which neglects the
297 axial and radial inhomogeneity that may be present in the real device.

298 The agreement with minor species (ethylene, acetylene and other unsaturated species) is generally
299 satisfactory. A systematic deviation is the over-prediction of C₄H₈ formation compensated by an under-
300 prediction in C₄H₄ concentration. As mentioned, a direct comparison for C₁₀H₈ experimental and
301 model profiles is not possible, as the real fuel already contains some naphthalene, not present in the
302 surrogate (the representative species adopted to match the di-aromatics content in the surrogates is α -
303 methyl-naphthalene). Despite the difference in the initial concentration, the model captures the timing
304 of naphthalene formation and its consumption. The entity of naphthalene formation (i.e., the delta
305 between the initial value and the peak value) is still well reproduced. The overall agreement at lean
306 conditions is generally satisfactory.

Compositional effects of SAFs

307 At rich conditions (Figure 7) the model/experiment comparisons show similar features. However, it
308 appears that the model presents more abrupt variations in the concentrations of some species, even
309 though the peaks are generally captured correctly. The experimental and modeling results are, however,
310 comparable to the ones obtained for other fuels previously tested on the same rig and simulations
311 performed using other kinetic models. These deviations appear to be somewhat systematic for the
312 stoichiometry condition here considered ($\phi=1.2$). More fuel-rich conditions seem to be captured by
313 most models significantly better. Further analysis will focus on understanding if these discrepancies
314 are the results of deviations from the plug flow reactor hypothesis used in the simulations or actual
315 deficiencies in the model.

316 **3.2 Fuel B1**

317 Figures 8 and 9 show the comparisons between calculations and experiments for Jet fuel B1 (ATJ).
318 When compared with the other two fuels, fuel B1 shows an earlier onset of the reactivity. This shows
319 in the form of an early initial drop in the oxygen concentration associated with the formation of
320 formaldehyde. It should be noted that B1 fuel was simulated using a two component surrogate
321 formulated from compositional information only, and the chemical composition of the fuel used in the
322 experiment matches almost perfectly the composition of the surrogate. Fuel simplicity eases the
323 surrogate formulation step, leaving all the weight of the discrepancies on the kinetic mechanism. As
324 the B1 mixture is composed largely of iso-dodecane, the simulation results are strongly dependent on
325 how accurate its model is. The CRECK mechanism for iso-dodecane has been developed applying the
326 analogy rules introduced in section 2.2.1, using the mechanism of iso-octane (a widely studied fuel
327 sharing strong structural similarities) as reference for the reaction rates. Unfortunately, experimental
328 data available for the validation of the iso-dodecane kinetic model are still somewhat limited, and no
329 speciation data were available at the time of the model formulation. Future works will focus on the
330 refinement of the iso-dodecane model, also including data from Gutzman et al. [34].

331 Despite the limited validation, the agreement with the flow reactor data obtained for this fuel is
332 comparable with what seen for the A1 fuel, confirming, at least in this instance, that reasonably accurate
333 models can be built starting from the fundamentals even in the absence of extensive validation data.
334 Notably, both the experiments and the simulations show that this fuel produces a very limited amount
335 of soot precursors (e.g., C_6H_6 , $C_{10}H_8$) even at slightly rich conditions.

336 **3.3 Fuel C1**

337 Figures 10 and 11 show the comparisons between calculations and experiments for the C1 fuel (the
338 high aromatic content fuel). The agreement with the experimental data is satisfactory also in this case,
339 even though the same issues that plague fuel A1 at rich conditions can be observed. The presence of
340 naphthalene in the fuel (not in the surrogate) is particularly evident here, but the $C_{10}H_8$ peak ends up
341 being relatively close to the experimental one and the consumption temperature is well captured.

342 **3.4 Relative behavior of the three fuels**

343 The last set of comparisons shown in figure 12 focuses on the relative behavior of the three fuels at
344 lean conditions. The model captures very well the differences in reactivity highlighted by the drop in

Compositional effects of SAFs

345 the O₂ concentration and the sharp rise in water. Fuel B1 appears to be the most refractory to high
346 temperature oxidation at the conditions of the flow reactor. The high aromatic content fuel is the second
347 least reactive and, compared with the other fuels, produces a lower amount of water, compatibly with
348 his lower H/C ratio. In terms of oxidation products, fuel B1 oxidation starts at lower temperature with
349 an early formation of CH₂O. The shape and magnitude of the CH₄ and CH₂O peaks are captured
350 correctly by the model, which also hints at their earlier formation.

351 Finally, the last row of Figure 12 highlights the relative formation of C₆H₆ and C₁₀H₈ measured by the
352 experiments and predicted by the model. Beside the initial amount of naphthalene present in the fuel,
353 the model does a good job at reproducing the relative concentrations. Fuel B1 produces only very
354 limited amounts of benzene and naphthalene, while the high aromatic fuel, as expected, is the most
355 prone to the formation of aromatic rings. These results could be correlated to the sooting tendencies of
356 the three fuels as the formation of mono- and, later, di-aromatics is the first step along the growth of
357 larger PAHs and soot. The ability of the model to capture the differences in reactivity and the relative
358 selectivity to products reinforces the idea that, in future analyses, a modeling grounded approach based
359 on composition-based surrogates and detailed kinetics can be used to predict the combustion behavior
360 of novel fuels, assisting the certification process of fuel candidates.

361 4 Conclusions

362 This paper describes the procedures used to characterize the reactivity of three representative jet fuels
363 from the fuel palette selected by the JETSCREEN program. A standard Jet fuel, an ATJ fuel and a high
364 aromatic content fuel were investigated experimentally and numerically in a flow reactor at
365 temperatures in the 800-1150K range and two fuel air ratios ($\Phi=0.8$ and 1.2) at atmospheric pressure.
366 Semi-detailed models reproducing the oxidation mechanism of the fuels were developed by coupling
367 the CRECK chemical kinetic model and a customized numerical tool for the formulation of fuel
368 surrogates. Comparisons of the experimental data collected by DLR were used to validate the model
369 and support the analysis of the combustion behavior.

370 From the numerical and experimental results it is possible to conclude that the general modeling
371 framework can capture major combustion characteristics of the real fuels and reproduce with good
372 accuracy the selectivity towards different intermediates during the oxidation of the real fuels. It is
373 evident that the fuel with the highest aromatic content has a significantly greater tendency to form soot
374 precursors, while the ATJ fuel (B1) has the least one. The high temperature reactivity of the ATJ is
375 also reduced compared to a traditional Jet A-1 (A1). The intermediate species peaks for the ATJ extend
376 to higher temperatures compared to the ones of the two fossil-based fuels (A1 and C1). Moreover, fuel
377 B1 (ATJ) also presents an earlier onset of the oxygen (and fuel) consumption, associated with the
378 formation of formaldehyde.

379 From a modelling perspective, it emerged that more validation is needed for some of the compounds
380 used in the surrogate palette, particularly for the aromatic and naphthenic fractions. Recently published
381 data may also offer the opportunity for improving the current iso-dodecane model. Because of the
382 entanglements introduced when considering complex mixtures, these experiments are not generally
383 suitable for the validation of specific submodels, although it is fair to conclude that some systematic

Compositional effects of SAFs

384 discrepancies may be related to deficiencies in the kinetic model. The simulations consistently
385 underestimate the formation of C₄H₈ in favor of more dehydrogenated species (C₄H₄), pointing to
386 inaccuracies in the oxidation and pyrolysis of small species. This mechanism may influence soot
387 growth phenomena, since strongly unsaturated linear species are prone to condensation reactions
388 leading to PAHs.

389 Moreover, for fuels with similarities to the high aromatic fuel C1, more components (high molecular
390 weight ones, in particular) may be needed to capture both the chemical and physical properties of the
391 target fuel (e.g., its distillation curve). While n-alkanes have been extensively studied in well-
392 characterized reacting systems (e.g., flow reactor, jet-stirred reactors, shock-tubes), data for high
393 molecular weight alkyl-aromatics and alkyl-cycloalkanes are more scarce, as their low volatility,
394 combined with their slower reactivity, makes their probing more challenging. In the absence of data,
395 models can only be constructed based on similarity rules, as described in the kinetic model section,
396 leading to higher uncertainties. Therefore, further research will have to locate the optimum between
397 uncertainties in the surrogate formulations and in the kinetic model of the components it contains.

398 5 References

- 399 [1] “Waypoint 2050.” [https://aviationbenefits.org/environmental-efficiency/climate-](https://aviationbenefits.org/environmental-efficiency/climate-action/waypoint-2050/)
400 [action/waypoint-2050/](https://aviationbenefits.org/environmental-efficiency/climate-action/waypoint-2050/) (accessed Jan. 14, 2022).
- 401 [2] “JET Fuel SCREENing and Optimization | JETSCREEN Project | Fact Sheet | H2020 | CORDIS |
402 European Commission.” <https://cordis.europa.eu/project/id/723525> (accessed Jan. 14, 2022).
- 403 [3] M. Pelucchi, P. Oßwald, W. Pejpichestakul, A. Frassoldati, and M. Mehl, “On the combustion
404 and sooting behavior of standard and hydro-treated jet fuels: An experimental and modeling
405 study on the compositional effects,” *Proc. Combust. Inst.*, vol. 38, no. 1, pp. 523–532, Gennaio
406 2021, doi: 10.1016/j.proci.2020.06.353.
- 407 [4] S. Dooley *et al.*, “A jet fuel surrogate formulated by real fuel properties,” *Combust. Flame*, vol.
408 157, no. 12, pp. 2333–2339, Dicembre 2010, doi: 10.1016/j.combustflame.2010.07.001.
- 409 [5] D. J. Luning Prak, G. R. Simms, T. Dickerson, A. McDaniel, and J. S. Cowart, “Formulation of 7-
410 Component Surrogate Mixtures for Military Jet Fuel and Testing in Diesel Engine,” *ACS Omega*,
411 Jan. 2022, doi: 10.1021/acsomega.1c05904.
- 412 [6] D. Kim, J. Martz, and A. Violi, “A surrogate for emulating the physical and chemical properties
413 of conventional jet fuel,” *Combust. Flame*, vol. 161, no. 6, pp. 1489–1498, Giugno 2014, doi:
414 10.1016/j.combustflame.2013.12.015.
- 415 [7] Y.-X. Liu, S. Richter, C. Naumann, M. Braun-Unkhoff, and Z.-Y. Tian, “Combustion study of a
416 surrogate jet fuel,” *Combust. Flame*, vol. 202, pp. 252–261, 2019, doi:
417 10.1016/j.combustflame.2019.01.022.
- 418 [8] M. Saffaripour, A. Veshkini, M. Kholghy, and M. J. Thomson, “Experimental investigation and
419 detailed modeling of soot aggregate formation and size distribution in laminar coflow diffusion
420 flames of Jet A-1, a synthetic kerosene, and n-decane,” *Combust. Flame*, vol. 161, no. 3, pp.
421 848–863, Mar. 2014, doi: 10.1016/j.combustflame.2013.10.016.

Compositional effects of SAFs

- 422 [9] A.-D. Martinos, N. Zarzalis, and S.-R. Harth, "Analysis of Ignition Processes at Combustors for
423 Aero Engines at High Altitude Conditions With and Without Effusion Cooling," presented at the
424 ASME Turbo Expo 2020: Turbomachinery Technical Conference and Exposition, Jan. 2021. doi:
425 10.1115/GT2020-16173.
- 426 [10] T. Yi, E. J. Gutmark, and B. K. Walker, "Stability and Control of Lean Blowout in Chemical
427 Kinetics-Controlled Combustion Systems," *Combust. Sci. Technol.*, vol. 181, no. 2, pp. 226–244,
428 Gennaio 2009, doi: 10.1080/00102200802424559.
- 429 [11] N. Rock *et al.*, "Lean Blowout Studies," in *Fuel Effects on Operability of Aircraft Gas Turbine
430 Combustors*, American Institute of Aeronautics and Astronautics, Inc., 2021, pp. 143–196. doi:
431 10.2514/5.9781624106040.0143.0196.
- 432 [12] P. Oßwald and M. Köhler, "An atmospheric pressure high-temperature laminar flow reactor for
433 investigation of combustion and related gas phase reaction systems," *Rev. Sci. Instrum.*, vol.
434 86, no. 10, p. 105109, Oct. 2015, doi: 10.1063/1.4932608.
- 435 [13] M. Köhler, P. Oßwald, D. Krueger, and R. Whitside, "Combustion Chemistry of Fuels:
436 Quantitative Speciation Data Obtained from an Atmospheric High-temperature Flow Reactor
437 with Coupled Molecular-beam Mass Spectrometer," *J. Vis. Exp.*, no. 132, Feb. 2018, doi:
438 10.3791/56965.
- 439 [14] T. Bierkandt, P. Oßwald, T. Schripp, and M. Köhler, "Experimental Investigation of Soot
440 Oxidation under Well-Controlled Conditions in a High-Temperature Flow Reactor," *Combust.
441 Sci. Technol.*, pp. 1–21, Mar. 2019, doi: 10.1080/00102202.2018.1554651.
- 442 [15] T.-C. Chu, Z. J. Buras, P. Oßwald, M. Liu, M. J. Goldman, and W. H. Green, "Modeling of
443 aromatics formation in fuel-rich methane oxy-combustion with an automatically generated
444 pressure-dependent mechanism," *Phys. Chem. Chem. Phys.*, vol. 21, no. 2, pp. 813–832, Jan.
445 2019, doi: 10.1039/C8CP06097E.
- 446 [16] T. Kathrotia, C. Naumann, P. Oßwald, M. Köhler, and U. Riedel, "Kinetics of Ethylene Glycol:
447 The first validated reaction scheme and first measurements of ignition delay times and
448 speciation data," *Combust. Flame*, vol. 179, pp. 172–184, May 2017, doi:
449 10.1016/J.COMBUSTFLAME.2017.01.018.
- 450 [17] F. Herrmann, P. Oßwald, and K. Kohse-Höinghaus, "Mass spectrometric investigation of the
451 low-temperature dimethyl ether oxidation in an atmospheric pressure laminar flow reactor,"
452 *Proc. Combust. Inst.*, vol. 34, no. 1, pp. 771–778, Jan. 2013, doi: 10.1016/J.PROCI.2012.06.136.
- 453 [18] M. Schenk *et al.*, "Detailed mass spectrometric and modeling study of isomeric butene
454 flames," *Combust. Flame*, vol. 160, no. 3, pp. 487–503, Mar. 2013, doi:
455 10.1016/J.COMBUSTFLAME.2012.10.023.
- 456 [19] P. Oßwald *et al.*, "Combustion kinetics of alternative jet fuels, Part-I: Experimental flow reactor
457 study," *Fuel*, vol. 302, 2021, doi: 10.1016/j.fuel.2021.120735.
- 458 [20] T. Schripp *et al.*, "Impact of Alternative Jet Fuels on Engine Exhaust Composition During the
459 2015 ECLIF Ground-Based Measurements Campaign," *Environ. Sci. Technol.*, vol. 52, no. 8, pp.
460 4969–4978, Apr. 2018, doi: 10.1021/acs.est.7b06244.
- 461 [21] E. Ranzi, M. Dente, A. Goldaniga, G. Bozzano, and T. Faravelli, "Lumping procedures in detailed
462 kinetic modeling of gasification, pyrolysis, partial oxidation and combustion of hydrocarbon

Compositional effects of SAFs

- 463 mixtures," *Prog. Energy Combust. Sci.*, vol. 27, no. 1, pp. 99–139, Gennaio 2001, doi:
464 10.1016/S0360-1285(00)00013-7.
- 465 [22] W. Pejpichestakul *et al.*, "Examination of a soot model in premixed laminar flames at fuel-rich
466 conditions," *Proc. Combust. Inst.*, vol. 37, no. 1, pp. 1013–1021, Jan. 2019, doi:
467 10.1016/J.PROCI.2018.06.104.
- 468 [23] W. K. Metcalfe, S. M. Burke, S. S. Ahmed, and H. J. Curran, "A Hierarchical and Comparative
469 Kinetic Modeling Study of C₁ – C₂ Hydrocarbon and Oxygenated Fuels," *Int. J. Chem. Kinet.*,
470 vol. 45, no. 10, pp. 638–675, Oct. 2013, doi: 10.1002/kin.20802.
- 471 [24] S. M. Burke *et al.*, "An experimental and modeling study of propene oxidation. Part 2: Ignition
472 delay time and flame speed measurements," *Combust. Flame*, vol. 162, no. 2, pp. 296–314,
473 Feb. 2015, doi: 10.1016/J.COMBUSTFLAME.2014.07.032.
- 474 [25] E. Ranzi, A. Frassoldati, A. Stagni, M. Pelucchi, A. Cuoci, and T. FARAVELLI, "Reduced Kinetic
475 Schemes of Complex Reaction Systems: Fossil and Biomass-Derived Transportation Fuels," *Int.*
476 *J. Chem. Kinet.*, vol. 46, no. 9, pp. 512–542, Sep. 2014, doi: 10.1002/kin.20867.
- 477 [26] E. Ranzi *et al.*, "Hierarchical and comparative kinetic modeling of laminar flame speeds of
478 hydrocarbon and oxygenated fuels," *Prog. Energy Combust. Sci.*, vol. 38, no. 4, pp. 468–501,
479 Aug. 2012, doi: 10.1016/J.PECS.2012.03.004.
- 480 [27] B. Ruscic, "Active Thermochemical Tables: Sequential Bond Dissociation Enthalpies of
481 Methane, Ethane, and Methanol and the Related Thermochemistry," *J. Phys. Chem. A*, vol.
482 119, no. 28, pp. 7810–7837, Jul. 2015, doi: 10.1021/acs.jpca.5b01346.
- 483 [28] A. Burcat and B. Ruscic, *Third millenium ideal gas and condensed phase thermochemical*
484 *database for combustion (with update from active thermochemical tables)*. Argonne, IL, 2005.
485 doi: 10.2172/925269.
- 486 [29] Z. Yu, S. Wei, C. Wu, L. Wu, L. Sun, and Z. Zhang, "Development and verification of RP-3
487 aviation kerosene surrogate fuel models using a genetic algorithm," *Fuel*, vol. 312, p. 122853,
488 Mar. 2022, doi: 10.1016/j.fuel.2021.122853.
- 489 [30] D. Kim and A. Violi, "Uncertainty-based weight determination for surrogate optimization,"
490 *Combust. Flame*, vol. 237, p. 111850, Mar. 2022, doi: 10.1016/j.combustflame.2021.111850.
- 491 [31] K. Narayanaswamy and P. Pepiot, "Simulation-driven formulation of transportation fuel
492 surrogates," *Combust. Theory Model.*, vol. 22, no. 5, pp. 883–897, Sep. 2018, doi:
493 10.1080/13647830.2018.1464210.
- 494 [32] C. L. Yaws, *The Yaws Handbook of Vapor Pressure : Antoine coefficients*.
- 495 [33] A. Cuoci, A. Frassoldati, T. Faravelli, and E. Ranzi, "OpenSMOKE++: An object-oriented
496 framework for the numerical modeling of reactive systems with detailed kinetic mechanisms,"
497 *Comput. Phys. Commun.*, vol. 192, pp. 237–264, Jul. 2015, doi: 10.1016/J.CPC.2015.02.014.
- 498 [34] J. Guzman, G. Kukkadapu, K. Brezinsky, and C. Westbrook, "Experimental and modeling study
499 of the pyrolysis and oxidation of an iso-paraffinic alcohol-to-jet fuel," *Combust. Flame*, vol.
500 201, pp. 57–64, Mar. 2019, doi: 10.1016/j.combustflame.2018.12.013.
- 501

502 6 List of Figures

503 **Figure 1: Schematic DLR high-temperature flow reactor and photographs from [12]. The**
504 **zoomed cutout shows a detailed view of the sampling interface and the ion source. Note that the**
505 **high-temperature oven is mounted on moveable rails and sampling is performed inside the tube**
506 **at ambient pressure**

507 **Figure 2: Major species profiles measured in the DLR high-temperature flow reactor**

508 **Figure 3: Soot precursor species measured at rich conditions ($\Phi = 1.2$)**

509 **Figure 4: Palette of candidate components for the formulation of modelling oriented surrogates**

510 **Figure 5: Measured distillation curves of the three fuels considered in the model (symbols) and**
511 **calculated equilibrium distillation curves of their surrogates**

512 **Figure 6: Comparison between measured (symbols) and calculated (lines) species profiles in the**
513 **DLR flow reactor: Fuel A1, $\Phi=0.8$. Series are labeled using matching colors**

514 **Figure 7: Comparison between measured (symbols) and calculated (lines) species profiles in the**
515 **DLR flow reactor: Fuel A1, $\Phi=1.2$. Series are labeled using matching colors**

516 **Figure 8: Comparison between measured (symbols) and calculated (lines) species profiles in the**
517 **DLR flow reactor: Fuel B1, $\Phi=0.8$. Series are labeled using matching colors**

518 **Figure 9: Comparison between measured (symbols) and calculated (lines) species profiles in the**
519 **DLR flow reactor: Fuel B1, $\Phi=1.2$. Series are labeled using matching colors**

520 **Figure 10: Comparison between measured (symbols) and calculated (lines) species profiles in the**
521 **DLR flow reactor: Fuel C1, $\Phi=0.8$. Series are labeled using matching colors**

522 **Figure 11: Comparison between measured (symbols) and calculated (lines) species profiles in the**
523 **DLR flow reactor: Fuel C1, $\Phi=1.2$. Series are labeled using matching colors**

524 **Figure12: Relative selectivity of the three fuels towards their oxidation intermediates at $\Phi=0.8$,**
525 **experiments (left) and calculations (right)**

526

527

528

529

530

531

532

533

534

Compositional effects of SAFs

535 **7 Conflict of Interest**

536 *The authors declare that the research was conducted in the absence of any commercial or financial*
537 *relationships that could be construed as a potential conflict of interest.*

538 **8 Funding**

539 This work was performed in the context of JetSCREEN, a project funded from the European Union's
540 Horizon 2020 research and innovation program under agreement No. 723525 .

541 **9 Tables**

Composition	A1	B1	C1
normal paraffins	19.2	0	10.1
iso-paraffins	30.7	99.9	15
monocyclic paraffins	21.8	0.1	16.4
polycyclic paraffins	8	0	33.8
mono aromatics	15.5	0	1.9
naphto aromatics	2.9	0	2.9
di-aromatics	1.8	0	19.9
H/C	1.94	2.152	1.718
MW [kg/kmol]	150	180	182
Density [kg/m ³]	786.8	756.4	858.1

542 **Table 1: Mass composition (%mass), H/C ratio, average molecular weight and density of the**
 543 **three fuels**

544

545

Fuel		A1	B1	C1
Hydrogen	[wt-%]	14.022	15.275	12.689
Uncertainty (SD)	[wt-%]	0.024	0.003	0.026
Fuel	[mg/min]	31.16	31.62	30.69
O ₂ lean	[mg/min]	132.6	137.1	127.9
O ₂ rich	[mg/min]	88.4	91.4	85.2

546 **Table 2: Inlet conditions and H-content. 17.64 g/min Ar diluent added at all conditions.**

547

Compositional effects of SAFs

Composition	A1	B1	C1
n-dodecane	23.1		
iso-dodecane	25.4	87.1	9.0
iso-cetane	12.3	12.9	22.5
methylcyclohexane	14.0		20.1
decalin	9.4		29.2
tri-methylbenzene	13.9		1.7
methylnaphthalene	1.9		17.6
H/C	1.96	2.161	1.77
MW [kg/kmol]	147.1	175.6	141.6
Density [kg/m ³]	787	745.3	843

548

549 **Table 3: Mass composition (%mass) of the three jet fuel surrogates proposed in this work**

550