

# Optimization of comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry (GC×GC/TOF-MS) for conventional and alternative jet fuels analysis

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## Abstract:

Comprehensive two-dimensional gas chromatography and time-of-flight mass spectrometry (GC×GC/TOF-MS) has been used in group-type chemical compositional analyses of gas turbine fuel as this state-of-the-art technique enables a detailed output of fuel constituents. However, it is an unreasonable expectation for one set of operational parameters to yield optimal separation for every fuel type. The aim of this study was to optimize the operational parameters for conventional jet fuel (Jet A) and the alternative fuel Hydroprocessed Esters and Fatty Acids (HEFA) to achieve the most efficient separation. Response surface methodology was utilized in design of experiments. The parameters investigated were as follows: modulation time (3.5–7.5s), oven temperature ramp (1–8°C/min), secondary oven temperature offset (15–40°C), and carrier gas flow rate (1.0–1.5 mL/min). The optimum parameters for Jet A and its mixture with HEFA were discovered.

## 1. Introduction

Comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry (GC×GC/TOF-MS) is an analytical instrument that has been widely used for the analysis of complex conventional and synthetic fuels [1,2]. Two-dimensional gas chromatography (GC×GC) separates components based on their volatility and polarity. In order to achieve the optimal GC×GC separation, the

operational parameters such as the modulation time, modulation temperature, column polarity combination, column dimension, carrier gas flow rate, temperature programming rate, and detector parameter settings, play an important role [3]. The relationship between GC×GC separation and the operational parameters was investigated in previous studies, where the selected parameters were varied based on different response variables and test samples. Previous research defined the number of peaks (NOP) detected



in the chromatogram as the primary response variable [4,5]. Similarity value (SV) is assigned to each identified peak utilizing the National Institute of Standards and Technology (NIST) library. SV is a measurement of the proximity the collected peak resembles the library mass spectra [6]. A perfect match is identified with an SV value of 999. Multiple researchers have adopted a minimum threshold SV value of 700 to 750 for peaks to be reliably identified as a specific component and disregarded the peaks with an SV value below 700 [6,7].

In a similar study, a central composite design in essential oils separation was adopted using GCxGC and the following parameter were optimized: modulation time, discharge time, first and second column flow rates [8]. Another study expanded these parameters with the addition of oven temperature ramp for the separation of octyl- and nonylphenol isomers [9]. In a study of optimizing grape pesticides separation, ion source temperature, oven temperature ramp, modulation time, hot pulse duration, and secondary oven temperature offset were sequentially adjusted [10]. However, the one-parameter-at-a-time approach is not an ideal approach as this methodology ignores all the “parameters cross interactions”; hence, it leaves out a broad region of interactive response output that would not be achieved through independent setting adjustments [7].

In this study, the component separation was optimized using fuel samples – Jet A and its mixture with HEFA. The optimization criterion was chosen as the maximum NOP with a SV value of 700 or more. Response surface methodology (RSM) was implemented to explore combination of multiple GCxGC parameters and to optimize the cumulative effect on the response variable.

## 2. Material and methods

### 2.1. Materials

HEFA is an alternative aviation fuel blending component approved by ASTM D 7566 [11]. Jet A and HEFA were provided by the Wright-Patterson Air Force Base, Dayton, Ohio. HEFA was produced by Honeywell UOP with camelina as the feedstock. In this

work, HEFA refers to the 50:50 vol.% mixtures of HEFA and Jet A. n-Pentane was used as a solvent to dilute the fuel samples.

### 2.2. Two-dimensional gas chromatography (GCxGC)

Pegasus 4D GCxGC/TOF-MS system (LECO, St. Joseph, MI, USA) equipped with Agilent 6890 gas chromatograph (Palo Alto, CA, USA) with a secondary oven and non-moving quad-jet dual stage modulator was utilized. Liquid nitrogen was used for modulation, and helium as the carrier gas. The sample dilution ratio was 1:100. Separation was achieved using Rtx-50 (Restek, Bellefonte, PA, USA) first dimension column (30 m × 0.25 mm × 0.25 μm) and HP-5MS (Agilent, Santa Clara, CA, USA) second dimension column (2 m × 0.25 mm × 0.25 μm). The primary oven was programmed from 35 to 200 °C. The front inlet temperature was 260 °C with 20:1 split ratio. The ion source temperature was 200 °C and the filament bias was -70 V. The mass range collected was 50–900 u with an acquisition rate of 250 spectra/s. Chroma-TOF software versions 2.32 and 3.4 were used for mass spectra collection and data processing (NIST 2014), respectively.

### 2.3. Optimization Aspects

Columns and scan rate (250 Hz) were kept constant during the experiments. Column selection was based on similar work in literature [12]. Experimental parameters investigated, in order to optimize the component separation in Jet A and HEFA samples, were as follows: 3.5–7.5 s modulation time, 1–8 °C/min oven temperature ramp, 15–40 °C secondary oven temperature offset, and 1.0–1.5 mL/min carrier gas flow rate.

### 2.3. Design of Experiment

The optimal fuel separation into its constituent components may not be achieved by the one-parameter-at-a-time approach, as multiple cross interactions between the operational parameters are possible. To address this challenge, RSM was used to simultaneously explore the functional relationships between the parameters and the response variable with the goal to optimize the response. In this section,

the sequential procedures of RSM and experimental design will be described. Further details may be found in literature [13-15].

RSM procedure was initiated from approximating a surface of response (NOP) over a parameter value region. The region of parameters was chosen based on preliminary experiments and literature. The procedure started from an approximation using a hyper-plane described by the following model:

$$Y = \mu + \sum_{i=1}^4 \beta_{1i} X_i + \varepsilon \quad (1)$$

where the coefficients  $\beta$ s depict the linear effects of the parameters – modulation time, oven temperature ramp, secondary oven temperature offset, and carrier gas flow rate – denoted by  $X_1$  to  $X_4$ , respectively.  $\varepsilon$  denotes the random error.  $\mu$  is the intercept in such linear models that allows more accurate estimates of  $\beta$ . This model of hyper-plane provided the steepest ascent direction to enhance the NOP level. Multivariate calculus can prove that such direction is represented by the vector  $(\beta_{11}, \dots, \beta_{14})$ , where  $\beta_s$  are the estimates of the model coefficients, obtained by the least squares method. Once an initial region of parameters is analyzed, exploratory experimental runs may be executed along the steepest ascent direction (vector  $\hat{\beta}$ ) to improve the NOP response.

These exploratory runs enabled the emergence of a different parameter region that included the optimal

parameter settings. A more efficient optimization was achieved following the second-order model of the surface as provided below:

$$Y = \mu + \sum_{i=1}^4 (\beta_{1i} X_i + \beta_{2i} X_i^2) + \sum_{i=1}^3 \sum_{j=i+1}^4 \gamma_{ij} X_i X_j + \varepsilon \quad (2)$$

This model allowed curved approximation and possible interaction effects represented by  $X_i^2$  and  $X_i X_j$ , respectively. Optimal combination of parameter settings was chosen by conducting another set of experiments over the new region. This new region was empirically confirmed via experimental runs.

Central composite design and Box-Behnken design are the two most common options for RSM [14]. However, the number of runs required for either optimization method may become excessive. Therefore, a flexible Custom Design platform available in SAS JMP software was utilized as this platform was previously reported to yield satisfactory results [16]. This optimization technique utilizes the coordinate-exchange algorithm to construct an optimal design with a manageable number of experimental runs for the user-specified model conditions [17]. The algorithm starts with a design whose parameter levels are randomly chosen within the feasible parameter region; and then it iteratively updates the parameters for the optimal design [17,18].

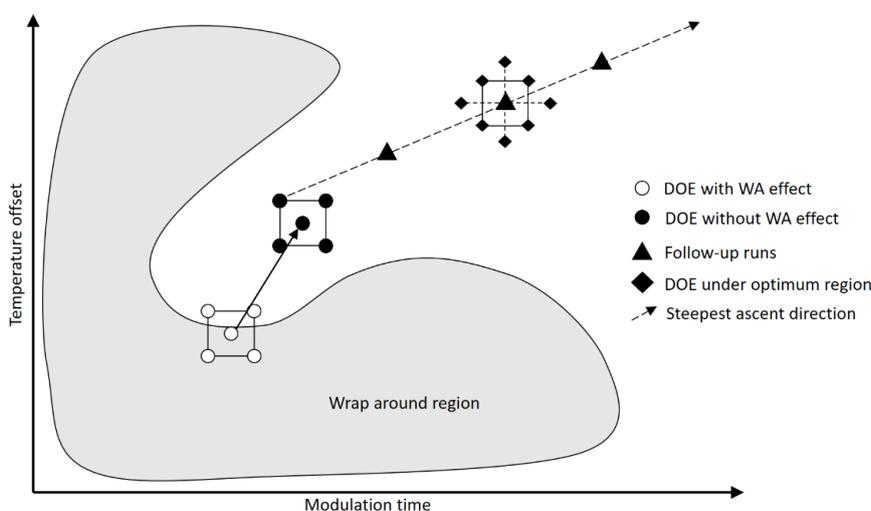


Figure 1. Simplified scenario with two parameters: modulation time and secondary oven temperature offset, where DOE denotes design of experiments and WA wrap-around

Figure 1 is a simplified illustration with only two parameters – modulation time and secondary oven temperature offset for this optimization process. The shaded area shows the parameter region that should be avoided in designing the experiments. The borders of this area were unknown in the initial iterative process. Each step in the optimization process added to the final shape. Therefore, it is possible to have selected design parameters that fall within this area as seen on Figure 1.

### 3. Results and Discussion

#### 3.1. Materials

Detailed chemical composition of Jet A can be found elsewhere [2]. In summary, Jet A was composed of all main hydrocarbon classes, such as n-paraffins, iso-paraffins, mono-cycloparaffins, di-cycloparaffins, mono-aromatics, di-aromatics, and cycloaromatics. Neat HEFA is composed almost exclusively of n-paraffins (ca 10 vol.%) and iso-paraffins (ca 85 vol.%) with a minor amount of cycloparaffins [19]. Therefore, HEFA/Jet A blend (50:50 vol.%) contained also all main hydrocarbon classes.

When Jet A was mixed with HEFA some of the compounds with low concentration were diluted resulting in lower concentrations than detectable by GCxGC/TOF-MS. For example, if Jet A contained 1.5 vol.% of di-aromatics and neat HEFA none, the resultant concentration was 0.75 vol.% causing a loss

of sensitivity due to dilution. Consequently, HEFA samples contained less peaks than Jet A.

#### 3.2. Optimization Aspects

The parameters investigated through optimization of aviation fuel analyses were: modulation time, oven temperature ramp, secondary oven temperature offset, and carrier gas flow rate. Out of this set, oven temperature ramp and helium flow rate affect the overall run time for the assay, the degree of separation in the first column, and the degree of separation in the second column. The modulation time affects the sharpness of chromatographic peaks, but at a cost of lower sensitivity [20]. Temperature offset has an effect on second dimension peak wrap-around (WA) effect [21-22].

WA effect appears when a component secondary retention time (RT) is longer than the modulation time [23-25]. Wrapped peaks may interfere with an accurate analysis only when WA effect causes overlapping with the constituent peaks in cases of which it should be avoided [12,22,25-27]. Other times this effect may even enable a better separation as it brings a more effective utilization of column space [12,27-28]. Therefore, WA effect is not always undesirable, unless wrapped peaks coelute with other peaks. In this study, WA effect was undesirable as it caused a disruptive outcome; therefore, chromatograms with WA were disregarded.

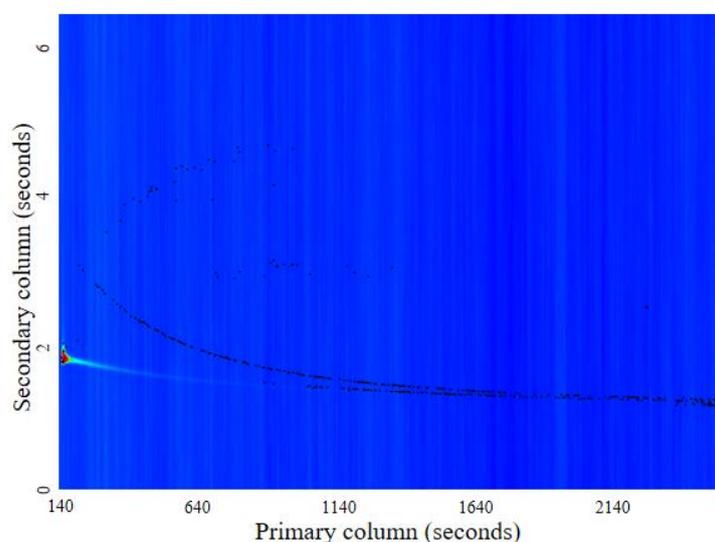


Figure 2. Gas chromatogram of n-pentane (R.T. 165, 1.48 s)

Figure 2 shows the two-dimensional gas chromatogram of n-pentane (solvent). Each black dot represents one specific compound (peak). On Figure 2, the only visible peak (RT 165, 1.48 s) is n-pentane and the number of compounds in the hyperbolic

shape (~160 s until the end of the run) is the column bleed. Figure 3 shows an example of WA effect from HEFA sample, which suggests a serious co-elution between compounds in the sample.

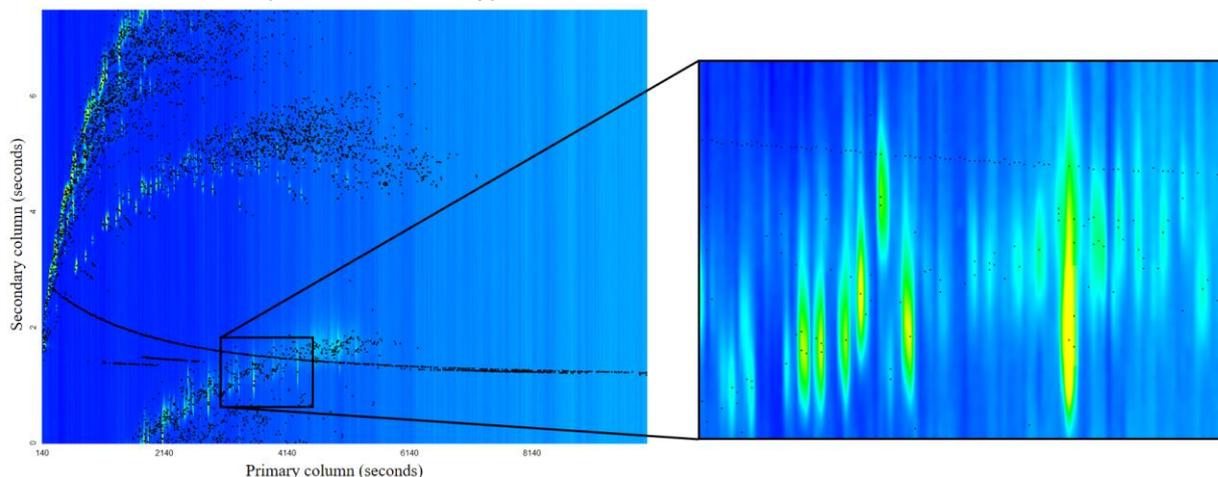


Figure 3. Gas chromatogram of HEFA sample (H-D2-R6, Table 2) with co-eluted wrapped peaks

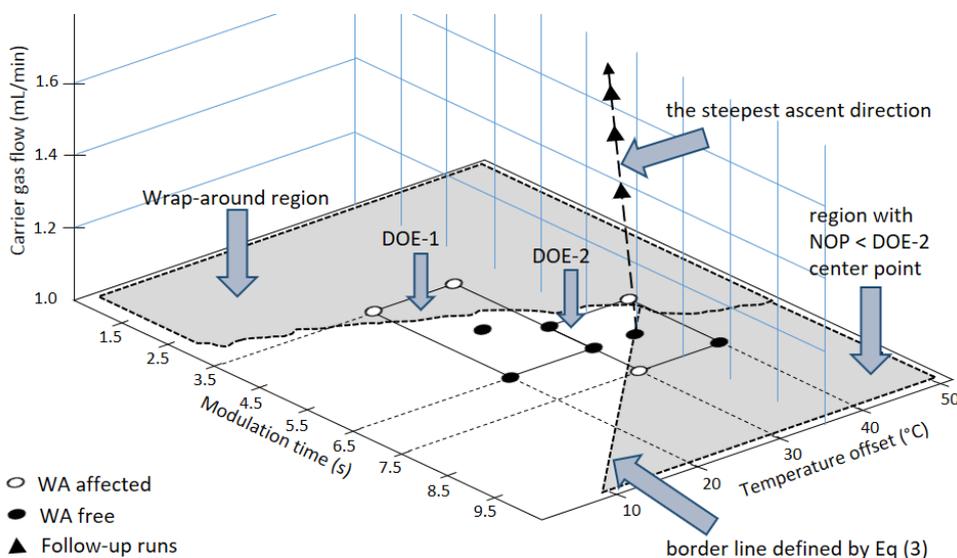


Figure 4. Three-dimensional (modulation time, temperature offset, and carrier gas flow) model of experiments containing DOE-1, DOE-2, and Follow-up runs

### 3.3. Design of Experiment

The statistical design of experiments utilized in this study included three tiers (DOE-1, DOE-2, and DOE-3). The initial design (referred to as DOE-1) for the model eq (1) covered the following parameter settings: 3.5–6.5 s modulation time, 2–4 °C/min oven temperature ramp, 20–30 °C secondary oven temperature offset, and 1.0–1.4 mL/min carrier gas

flow rate. It is important to note here that this optimization process is iterative; hence, it involves multiple trials of experimental values.

A majority of the DOE-1 runs showed WA effect that prevented the development of an acceptable model fitting. The DOE-1 parameter region tested overlapped with the WA area which should be avoided, as illustrated in Figure 1. The parameter



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impacts on WA effects were evaluated to find another region. For instance, WA phenomenon occurred when the specified modulation period is shorter than the second dimension RT that some compounds needed. As a result, those compounds were “wrapped” and only detected in the following

modulation cycle. Moreover, previous studies increased oven temperature offset to avoid WA [21,22]. These analyses guided the design of a second set of experiments (called DOE-2) where longer modulation times and different temperature offset settings were utilized.

Table 1. Second Stage Design of Experiment for Jet A (DOE-2 Jet A)

| Run Index | Modulation Time (s) | Temp. Ramp (°C/min) | Temp. Offset (°C) | Flow Rate (mL/min) | NOP  | WA  |
|-----------|---------------------|---------------------|-------------------|--------------------|------|-----|
| J-D2-R1   | 5.5                 | 3                   | 30                | 1.0                | 1970 | No  |
| J-D2-R2*  | 6.5                 | 2                   | 35                | 1.1                | 2223 | No  |
| J-D2-R3   | 7.5                 | 3                   | 40                | 1.0                | 1582 | No  |
| J-D2-R4   | 5.5                 | 1                   | 40                | 1.0                | 2510 | Yes |
| J-D2-R5   | 5.5                 | 1                   | 30                | 1.2                | 2355 | Yes |
| J-D2-R6   | 7.5                 | 1                   | 30                | 1.0                | 2435 | Yes |
| J-D2-R7   | 5.5                 | 3                   | 40                | 1.2                | 1902 | No  |
| J-D2-R8   | 7.5                 | 1                   | 40                | 1.2                | 2439 | No  |
| J-D2-R9*  | 6.5                 | 2                   | 35                | 1.1                | 2310 | No  |
| J-D2-R10  | 7.5                 | 3                   | 30                | 1.2                | 1845 | No  |
| J-D2-R11* | 6.5                 | 2                   | 35                | 1.1                | 2435 | No  |

\*Center point of the design

Table 2. Second Stage Design of Experiment for HEFA (DOE-2 HEFA)

| Run Index | Modulation Time (s) | Temp. Ramp (°C/min) | Temp. Offset (°C) | Flow Rate (mL/min) | NOP  | WA  |
|-----------|---------------------|---------------------|-------------------|--------------------|------|-----|
| H-D2-R1   | 5.5                 | 3                   | 30                | 1.0                | 1851 | No  |
| H-D2-R2*  | 6.5                 | 2                   | 35                | 1.1                | 2025 | No  |
| H-D2-R3   | 7.5                 | 3                   | 40                | 1.0                | 1558 | No  |
| H-D2-R4   | 5.5                 | 1                   | 40                | 1.0                | 2757 | Yes |
| H-D2-R5   | 5.5                 | 1                   | 30                | 1.2                | 2676 | Yes |
| H-D2-R6   | 7.5                 | 1                   | 30                | 1.0                | 2386 | Yes |
| H-D2-R7   | 5.5                 | 3                   | 40                | 1.2                | 1971 | No  |
| H-D2-R8   | 7.5                 | 1                   | 40                | 1.2                | 2507 | No  |
| H-D2-R9*  | 6.5                 | 2                   | 35                | 1.1                | 2228 | No  |
| H-D2-R10  | 7.5                 | 3                   | 30                | 1.2                | 1849 | No  |
| H-D2-R11* | 6.5                 | 2                   | 35                | 1.1                | 2172 | No  |

\*Center point of the design



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The DOE-2 experimental parameters were as follows: 5.5–7.5 s modulation time, 1–3 °C/min oven temperature ramp, 30–40°C secondary oven temperature offset, and 1.0–1.2 mL/min carrier gas flow rate. Results for DOE-2 are shown in Tables 1 and 2. Due to the fact HEFA was 50:50 vol.% blend

with Jet A, the same design of experiments was used. The highest WA effect free NOPs for Jet A and HEFA were obtained for runs J-D2-R8 and H-D2-R9, respectively. Data from DOE-2 were utilized to fit a linear model from eq (1) for Jet A and HEFA:

$$\hat{Y}_{\text{Jet A}} = 4341.64 - 128.98 X_1 - 432.93 X_2 - 20.10 X_3 + 310.25 X_4 \quad (3)$$

$$\hat{Y}_{\text{HEFA}} = 2572.68 - 98.15 X_1 - 354.95 X_2 - 7.43 X_3 + 1083.5 X_4 \quad (4)$$

where  $X_1$  to  $X_4$  were modulation time, oven temperature ramp, secondary oven temperature offset, and carrier gas flow rate, respectively. For instance, in eq (3) a one second increase in the modulation time ( $X_1$ ) is associated with 128.98 less NOP value.  $\hat{Y}$  is a function of  $X_1$  to  $X_4$ , and based on multivariate calculus, the steepest ascending direction is along the gradient vector, which is the vector  $\hat{\beta}$  when partial derivatives are taken.

mL/min carrier gas flow rate combined with the step size  $-0.01$  s,  $-0.05$  °C/min,  $0$  °C, and  $+0.15$  mL/min, respectively. Results for the Follow-up experiments displaying the parameter values are provided in Table 3. Figures 5 and 6 display the chromatograms obtained with DOE-2 and Follow-up parameters.

Along the direction of steepest ascent (represented by dashed arrows in Figures 1 and 4, Follow-up experiments were conducted to locate the region of the second-order model eq (2) based on the following criteria:

The standard deviations calculated from all replicates were 87.6 and 75.9 peaks for Jet A and HEFA, respectively. These values were approximation only and a higher accuracy can be obtained with more runs. The estimated standard deviation typically becomes smaller when there are more replicates. The highest NOPs for Jet A and HEFA were J-F-R2 (2553) and H-D2-R8 (2507), respectively. The NOP values for J-F-R2 and J-F-R3 were in close proximity. This finding suggested that the experiments conducted were within the optimal area for Jet A. Hence, this set of parameters was considered to be optimal. In this particular case for Jet A, the difference in NOP values obtained by exploring the DOE-3 area was predicted to be negligible given the potential standard deviation, associated costs, and time consumption. As for HEFA samples, the NOP values from Follow-up runs were lower than results from DOE-2 and the NOP of H-D2-R8 is very close to the high values in Jet A DOE-2 runs. This suggested H-D2-R8 parameters were optimal since we have noted that HEFA samples generally contain less peaks than Jet A. Further experiments in DOE-3 for HEFA is regarded as unnecessary given the costs and the minimal extra usefulness for general downstream analyses. Figure 4 shows a three-dimensional model of experiments that were utilized in this study (as opposed to the two-dimensional model given in Figure 1). For applying the second-

1. Set the starting point and incremental values (step size) utilizing DOE-2 results.
2. If the response  $\hat{Y}$  of the Follow-up run is greater than the preceding one, move further along the steepest ascent direction. and conduct the consecutive Follow-up run.
3. If the NOP is still higher, continue as in step 2. Otherwise, accept the latest set of parameters as the initial set of parameters for DOE-3.

The starting point for Jet A was the center point of DOE-2 (6.5 s modulation time, 2 °C/min oven temperature ramp, 35 °C secondary oven temperature offset, and 1.1 mL/min carrier gas flow rate). Step size was specified as  $-0.06$  s,  $-0.21$  °C/min,  $0$  °C, and  $+0.15$  mL/min, for the four operational parameters, by scaling the vector  $\hat{\beta}$  so that parameter values of the Follow-up runs are still feasible GCxGC experiments. Starting point for HEFA was selected as 6.5 s modulation time, 2 °C/min oven temperature ramp, 37 °C secondary oven temperature offset, and 1.14

order model eq (2) in DOE-3 region, further work would be required, consisting of following steps:

1. The region for DOE-3 experiment was chosen so that the Follow-up run or the DOE-2 run with the highest NOP was covered (J-F-R2 and H-D2-R8).
2. JMP software was utilized to design DOE-3; parameter values for each experiment are provided in Tables 4 and 5.

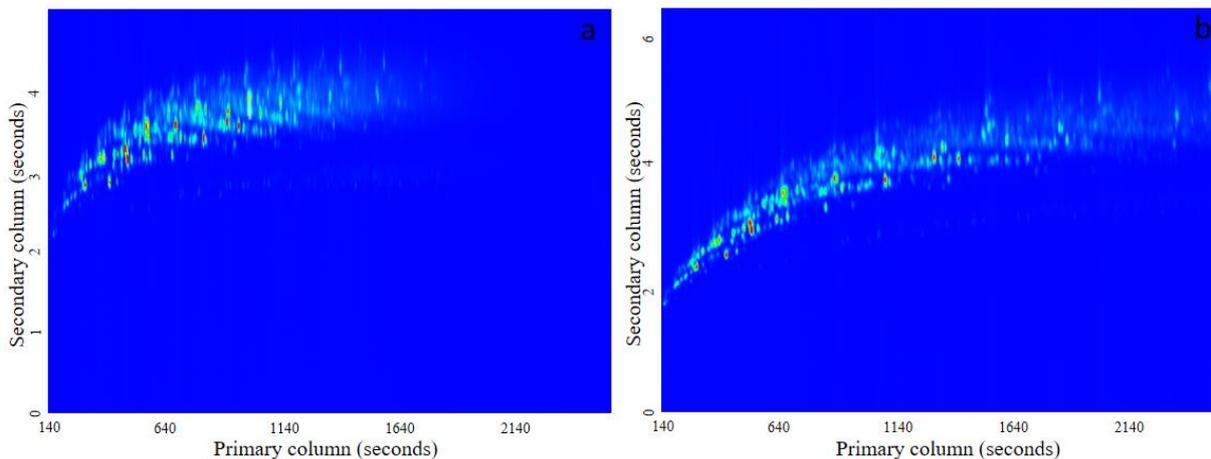


Figure 5. Chromatograms of Jet A: (a) J-D2-R1 (NOP 1970) and (b) optimal settings J-F-R2 (NOP 2553)

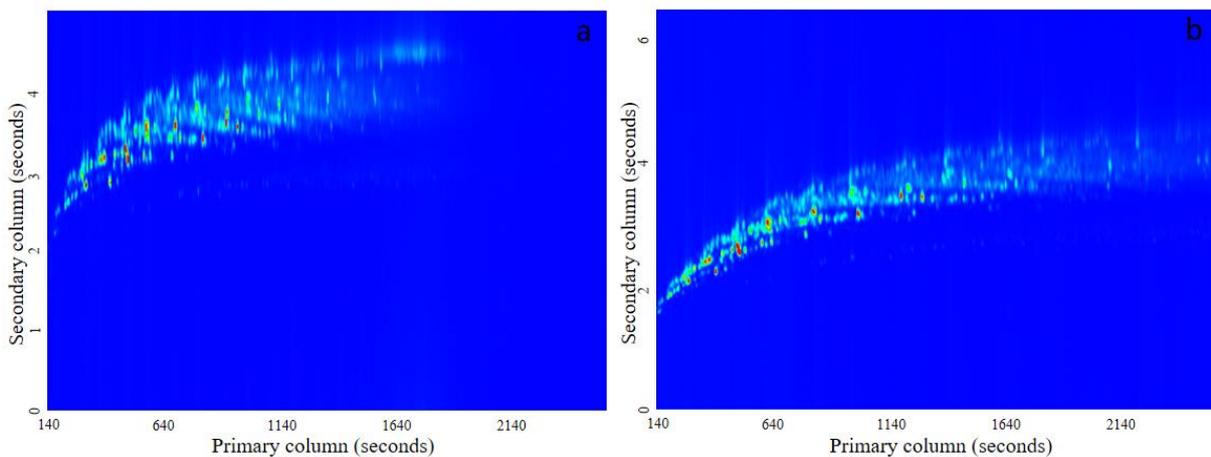


Figure 6. Chromatograms of HEFA: (a) H-D2-R8 (NOP 2507) and (b) optimal settings H-F-R3 (NOP 2247)

Table 3. Follow-up Experiment for Jet A and HEFA

| Run Index | Fuel  | Modulation Time (s) | Temp. Ramp (°C/min) | Temp. Offset (°C) | Flow Rate (mL/min) | NOP  | WA |
|-----------|-------|---------------------|---------------------|-------------------|--------------------|------|----|
| J-F-R1    | Jet A | 6.44                | 1.79                | 35                | 1.25               | 2480 | No |
| J-F-R2    | Jet A | 6.38                | 1.58                | 35                | 1.40               | 2553 | No |
| J-F-R3    | Jet A | 6.31                | 1.37                | 35                | 1.55               | 2550 | No |
| H-F-R1    | HEFA  | 6.49                | 1.95                | 37                | 1.29               | 2145 | No |
| H-F-R2    | HEFA  | 6.47                | 1.9                 | 37                | 1.44               | 2212 | No |



H-F-R3 HEFA 6.46 1.85 37 1.59 2247 No

**Table 4. Third Stage Design of Experiment for Jet A fuel (DOE-3 Jet A)**

| Run Index | Modulation Time (s) | Temp. Ramp (°C/min) | Temp. Offset (°C) | Flow Rate (mL/min) |
|-----------|---------------------|---------------------|-------------------|--------------------|
| J-D3-R1   | 6.51                | 1.4                 | 35                | 1.55               |
| J-D3-R2   | 6.38                | 1.58                | 36                | 1.55               |
| J-D3-R3   | 6.25                | 1.4                 | 35                | 1.25               |
| J-D3-R4   | 6.25                | 1.48                | 34                | 1.55               |
| J-D3-R5   | 6.51                | 1.4                 | 36                | 1.25               |
| J-D3-R6   | 6.25                | 1.76                | 36                | 1.4                |
| J-D3-R7   | 6.25                | 1.76                | 35                | 1.55               |
| J-D3-R8   | 6.25                | 1.58                | 36                | 1.25               |
| J-D3-R9   | 6.38                | 1.58                | 35                | 1.4                |
| J-D3-R10  | 6.25                | 1.76                | 34                | 1.29               |
| J-D3-R11  | 6.38                | 1.58                | 35                | 1.4                |
| J-D3-R12  | 6.25                | 1.4                 | 36                | 1.4                |
| J-D3-R13  | 6.51                | 1.76                | 35                | 1.55               |
| J-D3-R14  | 6.38                | 1.76                | 35                | 1.25               |
| J-D3-R15  | 6.51                | 1.76                | 36                | 1.4                |
| J-D3-R16  | 6.38                | 1.4                 | 34                | 1.4                |
| J-D3-R17  | 6.51                | 1.58                | 34                | 1.25               |
| J-D3-R18  | 6.51                | 1.58                | 35                | 1.4                |

#### 4. Conclusions

Comprehensive two-dimensional gas chromatography is a state-of-the-art instrument for the analyses of complex mixtures such as jet fuels. This study evaluated the instrumental conditions to optimize the GCxGC analytical method for Jet A and its mixture with HEFA using RSM. One crucial criterion of the experimental design was the avoidance of potential WA effect. The optimum parameter for Jet A were discovered to be: 6.3–6.4 s modulation time, 1.3–1.6 °C/min oven temperature ramp, 37 °C secondary oven temperature offset, and 1.40–1.55 mL/min carrier gas flow rate. The parameters for HEFA were discovered to be: 7.5 s modulation time, 1 °C/min oven temperature ramp, 40 °C secondary oven temperature

offset, and 1.2 mL/min carrier gas flow rate. The statistical method adopted in this study can be utilized for different types of GCxGC, columns, and samples. Furthermore, this method can be extended to more operational parameters.

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