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Flow Modulated Comprehensive Two-Dimensional Gas Chromatography

Part I - Low Duty Cycle Modulation of Hydroprocessed Vegetable Oil

Rodrigo Passini¹, Danilo Pierone², Angelo L. Gobbi¹, and Leandro W. Hantao^{1,3*} 

¹Laboratório Nacional de Nanotecnologia (LNNano), Centro Nacional de Pesquisa em Energia e Materiais (CNPEM), Polo II de Alta Tecnologia, R. Giuseppe Máximo Scolfaro, 10000 - 13083-970 Campinas SP Brazil

²Nova Analítica, Rua Assungui, 432 - 04131-000 São Paulo SP Brazil

³Instituto de Química, Universidade Estadual de Campinas, R. Josué de Castro, 126 - Cidade Universitária, 13083-861 Campinas SP Brazil

In this paper, we report the quantitation of hydroprocessed vegetable oil (HVO) in petroleum diesel and biodiesel blends. To accomplish this goal, we have developed a low-pressure interface using commercially available components from original equipment manufacturer (OEM) SGE / Trajan Scientific and Medical. The low duty cycle modulation was optimized using a multivariate approach by investigating three important parameters, namely, flush period, auxiliary gas flow, and dimension of restrictor capillary (*i.e.*, bleed). A 5-fold reduction in analysis time was accomplished, while maintaining the group-type separations by exploiting short modulation period. Successful quantitation of HVO was attained due to the inherent low sensitivity of the interface allowing for a wide linear range from 1.0% (w/w) to 100.0% (w/w). The current low pressure and low duty cycle interface exhibits simple and robust operation being particularly suited for fuel analysis.

Keywords: renewable fuel, petroleum, green chemistry, esters, fatty acids.

INTRODUCTION

The demand for cleaner burning and renewable motor fuels, alongside the high cost of petroleum, has drawn great interest in the production and distribution of alternative fuels [1]. Over the past decades, ethanol and biodiesel have been explored as alternative fuels. For instance, biodiesel is produced from the solvolysis of triglycerides using an alcohol and a catalyst [2]. Recently, hydro-processed vegetable oil (HVO) has been considered as a potential candidate for diesel engines, see Table I.

Table I. Main characteristics of hydro-processed vegetable oil (HVO)*

Renewable fuel generation	2 nd generation
Release year	2007 by Neste Oil Porvoo Refinery
Main producers	Neste Oil Porvoo Refinery (Finland), ConocoPhillips (USA), Universal Oil Products-Eni (UK, Italy), Nippon Oil (Japan), SK Energy (Korea), and Syntroleum (USA)
Commercial name and references	NExBTL, hydro-processed vegetable oil (HVO), hydro-processed esters and fatty acids (HEFA), renewable diesel fuel, hydrogenation derived renewable diesel, green diesel, hydrogen treating biodiesel (HBD)
Molecular formula	$C_n H_{2n+2}$
Benefits	High calorific value, high cetane number, oxidation stability, negligible aromatic and sulfur-compounds

*The interested reader is directed to Sonthalia, A.; Kumar, N. *J. Energy Inst.*, 2019, 92 (1), pp 1-17 (<https://doi.org/10.1016/j.joei.2017.10.008>) for the complete report.

The production of HVO also uses triglycerides as substrates, but it explores elevated temperatures and high hydrogen pressure to promote hydrogenation and cracking producing *n*-paraffins and *iso*-paraffins in the boiling point range of gasoline and diesel [2]. In Germany, 20% of common diesel fuels are already blended with HVO in percentages of approximately 7.7% (v/v) [3]. However, standard methods have not accompanied the changes in diesel blends using HVO, leading to a debate on the suitability of these analytical methods for quality analysis and quality control (QA/QC).

In this context, comprehensive two-dimensional gas chromatography (GC×GC) is the ideal technique for QA/QC of HVO in petroleum diesel / biodiesel blends providing unprecedented peak capacity and shorter chromatographic runs compared to conventional gas chromatography (1D-GC) [4]. The augmented resolving power of GC×GC arises from the sequential combination of two complementary GC separations with distinct selectivity. The two-dimensional separation is accomplished by coupling two GC columns interfaced by the modulator. The modulator is the core of the GC×GC instrument, being responsible for the continuous and periodical transference of solute bands from the first stage (¹D) to the second stage (²D) as narrow pulses. Thermal modulation [5,6] is the dominant principle in GC×GC, however it is also the main reason why such technique has not been adopted for routine analysis. For instance, the overhead cost associated with the coolant fluid, e.g. liquid nitrogen, represents a 19-fold increase in operational cost, while the use of working fluid, nitrogen gas, represents an additional 86% to the operating expenses for a GC×GC-FID.

Flow modulation, also referred to as flow-switching modulation, uses an auxiliary gas to actuate the vapor stream inside a microfluidic platform to attain modulation during GC×GC analysis [7]. The microfluidic devices are installed inside the GC oven, while an actuating valve is positioned outside the oven. Two alternating stages comprise flow modulation, namely, solute re-injection (flush) and accumulation (fill). Hence, flow modulation encompasses low-duty cycle [8] and full transfer interfaces (forward [9] and reverse fill/flush [10] configurations). A low-duty cycle interface is based on high-speed Deans Switch and typically exhibit much lower sensitivity, compared to full transfer modulators, since it lacks a sampling loop. Despite this drawback, the low-duty cycle flow-switching interface is likely the most robust and easy to operate modulator among all GC×GC solutions.

In this paper, we report the development of a low-duty cycle flow modulator using commercially available components from original equipment manufacturer (OEM) SGE / Trajan Scientific and Medical. The flow-switching interface was evaluated using experimental design to account for pure and interaction effects. Such semi-empirical model was used to determine the optimum experimental conditions for GC×GC modulation. Lastly, the quantitation of hydro-processed vegetable oil in petroleum diesel and biodiesel blends was performed.

MATERIALS AND METHODS

Samples: HVO, Biodiesel, and Diesel

Hydro-processed vegetal oil, NExBTL, was purchased from Neste Oil (Finland). Biodiesel and petroleum diesel, S10A, samples were provided by Petrobras SA (Brazil) [11]. The composition of the analytical solutions is described in Table II.

Table II. Calibration samples for determination of HVO in petroleum diesel / biodiesel blends

Sample	HVO % (v/v)	Diesel % (v/v)	Biodiesel % (v/v)
1	1.0	73.5	25.5
2	2.0	73.0	25.0
3	3.0	72.5	24.5
4	4.0	72.0	24.0
5	5.0	71.5	23.5
6	6.0	71.0	23.0

Table II. Calibration samples for determination of HVO in petroleum diesel / biodiesel blends (Cont.)

Sample	HVO % (v/v)	Diesel % (v/v)	Biodiesel % (v/v)
7	7.0	70.5	22.5
8	8.0	70.0	22.0
9	9.0	69.5	22.5
10	17	65.5	17.5
11	21	63.5	15.5
12	25	61.5	13.5
13	33	57.5	9.5
14	41	53.5	5.5
15	46	51.0	3.0
16	48	50.0	2.0
17	49	49.5	1.5
18	60	33.0	7.0
19	70	23.0	7.0
20	80	13.0	7.0
21	90	3.0	7.0
22	100	0.0	0.0

GC×GC-FID analyses

The GC×GC-FID system consisted of a TRACE 1310 GC-FID gas chromatograph (Thermo Fisher Scientific – Waltham, MA, USA) equipped with a split/splitless injector and a AS 1300 105-position autosampler. GC×GC separations were performed using a high-speed Deans switch modulator based on SilFlow platform (SGE Analytical– Victoria, Australia) as shown in Figure 1 [12,13].

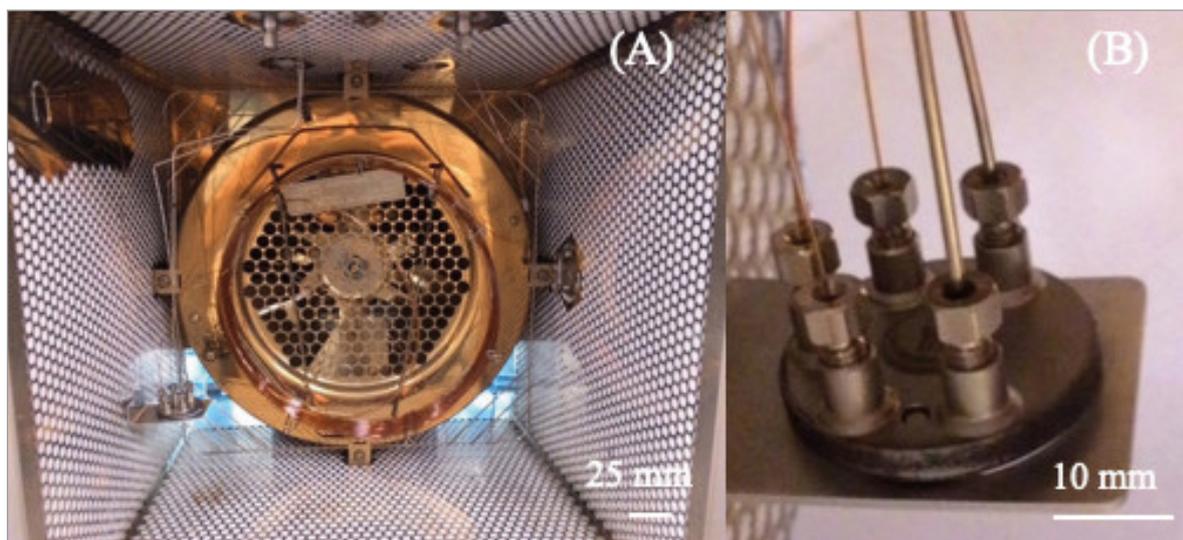


Figure 1. Low duty cycle flow switching modulator for comprehensive two-dimensional gas chromatography. In (A) the fast Deans Switching device is installed inside a TRACE 1310 GC (Thermo Scientific) highlighting the small footprint of the interface. The small footprint is important to ensure low thermal of the composite system. In (B) we illustrate the simple configuration of the interface for non-expert users.

The injector and detector were operated at 250 °C. A split ratio of 100:1 was used in the injection of 1 μ L of sample. Modulation period was set to 2.5 s. Column set comprised a 30 m \times 0.32 mm ID DB-5MS (0.25 μ m film thickness) primary column and a 2.0 m \times 0.25 mm MEGAWAX-HT (0.15 μ m film thickness) secondary column (MEGA srl – Megano, MI, Italy). The restriction capillary length was evaluated from 15 to 35 cm \times 0.25 mm ID. The independent variables evaluate in the experimental design were flush duration, auxiliary gas flow, and length of restrictor capillary.

RESULTS AND DISCUSSION

Flow switching modulation

In order to effectively exploit the improved peak capacity of GC \times GC separations two requisites are mandatory for low-duty cycle FM-GC \times GC. First, the chromatographic conditions must be optimized to produce a minimum modulation ratio (M_R) of 3 to ensure negligible variability from modulation [14]. This condition may be fulfilled by using short modulation periods (P_M) or highly retentive primary columns ($b < 250$), as shown in Equation 1. Secondly, we strongly recommend that the average 2w_b not exceed 15% of the value of P_M to provide usable separation space in the GC \times GC chromatograms.

$$M_R = 4 \frac{{}^1W_b}{P_M} \quad \text{Equation 1}$$

In practice the average peak width in the 2D is directly proportional to the reinjection pulse duration (P), and also to the flow in the 1D (1F) and 2D (2F), as shown in Equation 2. In Figure 2 we illustrate the impact of the injection pulse on the peak width of dodecane.

$${}^2w_b \propto P \frac{{}^1F}{{}^2F} \quad \text{Equation 2}$$

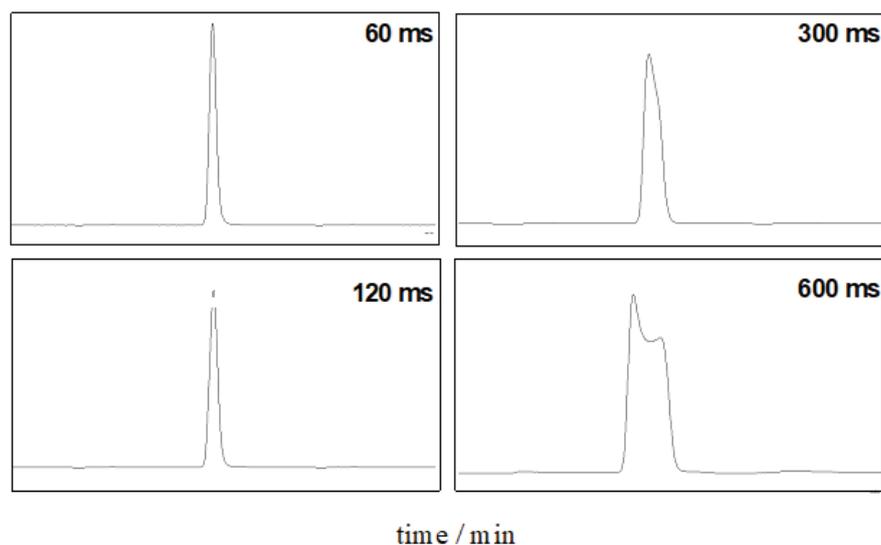


Figure 2. Impact of the injection pulse to peak profile of dodecane in low duty cycle flow switching modulation for comprehensive two-dimensional gas chromatography.

The efficiency of flow switching modulation is highly dependent on numerous chromatographic conditions. Three independent variables (*i.e.*, factors) are highlighted, namely, bleed capillary, auxiliary

flow, and reinjection pulse. Since the pneumatics of the composite system is easily influenced by each of these variables, a multivariate approach for method optimization is required. This approach, experimental design, is critical for empirical modelling of the modulator behavior because the independent variables may exhibit interaction effects in addition to the pure effects. Hence, a central composite design was assembled using the experiments shown in Table III.

Table III. Experimental design used to determine the optimum conditions for modulation of dodecane

Experiment	Coded			Original Value		
	X_1	X_2	X_3	Pulse / ms	Auxiliary gas / mL min ⁻¹	Bleed length / cm
1	-1	-1	-1	100	1.4	15
2	-1	-1	1	100	1.4	35
3	-1	1	-1	100	1.46	15
4	-1	1	1	100	1.46	35
5	1	-1	-1	140	1.4	15
6	1	-1	1	140	1.4	35
7	1	1	-1	140	1.46	15
8	1	1	1	140	1.46	35
12	-1.68	0	0	100	1.43	25
13	1.68	0	0	140	1.43	25
14	0	-1.68	0	120	1.4	25
15	0	1.68	0	120	1.46	25
16	0	0	-1.68	120	1.43	15
17	0	0	1.68	120	1.43	35
9	0	0	0	120	1.43	25
10	0	0	0	120	1.43	25
11	0	0	0	120	1.43	25

A central composite model was built using the asymmetry factor of dodecane. The probe solute, dodecane, was selected because it experiences small retention on the ²D. So, the average peak width may be used to evaluate the quality of the modulation conditions. As previously shown in Figure 2, poor modulation generates asymmetrical peak, so the asymmetry factor is a good parameter to monitor the performance of flow modulation. A response surface was plotted using the statistically valid model ($\alpha = 0.05$) as illustrated in Figure 3.

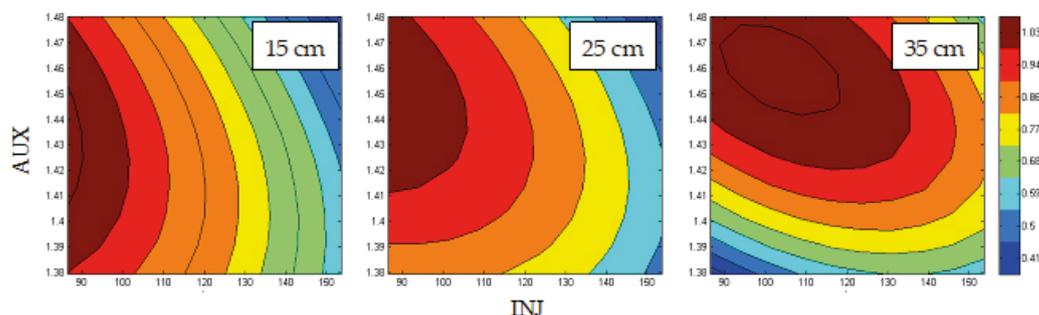


Figure 3. Response surface attained for low duty cycle flow switching modulation using the experimental design described in Table III.

Selection of the modulation conditions required that the value of peak asymmetry factor was approximately 1.0. Careful investigation of the response surface indicated that GC×GC analysis attained with 1.46 mL min⁻¹ of auxiliary gas, length of bleed capillary of 35 cm, and injection pulse of 120 ms produced the most symmetrical peak of dodecane. Noteworthy, this multivariate optimization protocol may be easily extended to full transfer interfaces for flow modulation, such as the forward fill/flush [15] and reverse fill/flush interfaces [16].

Quantitation of VGO in diesel/biodiesel blends

The optimized GC×GC method was initially used to screen petroleum diesel, biodiesel, and hydroprocessed vegetable oil. The chromatograms are shown in Figure 4. The GC×GC chromatogram of HVO clearly indicates that this particular sample exhibited numerous linear and branched hydrocarbons with a volatility range from *n*-C₆ to *n*-C₁₇. Also, the chromatographic profile of such sample further supports the absence of aromatic hydrocarbons in this renewable fuel. Inspection of nitrogen- and sulfur-containing compounds would require selective detectors or hyphenation to mass spectrometry, which was not the objective of this case study. In Figure 4 B is shown the GC×GC chromatogram of diesel/biodiesel blend. The cluster of monoaromatic hydrocarbons, which exhibit higher retention in the ²D, is readily seen in the chromatogram of diesel blend. Also, this diesel sample exhibited a pronounced unresolved complex mixture (UCM) profile in the volatility range from *n*-C₉ to *n*-C₁₆. Furthermore, the soy biodiesel is easily characterized by the two peaks with van den Dool and Kratz retention indices above 1700.

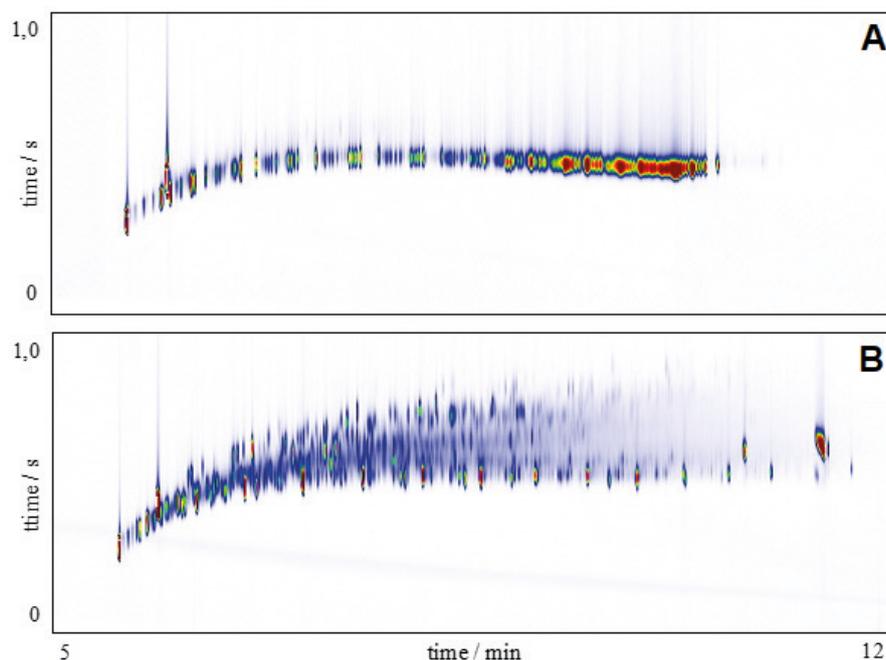


Figure 4. Flow-modulated comprehensive two-dimensional gas chromatography analysis of hydroprocessed vegetable oil (HVO) (A) and diesel/biodiesel blend (B).

In order to perform quantitation, a suitable analyte must be found that is both present in the HVO sample and absent in the diesel/biodiesel blend. In this case study, we have selected a branched paraffin adjacent to *n*-heptadecane with retention index of approximately 1770. This marker was ideal for this application as the UCM was pronounced in the volatility range of *n*-C₆ to *n*-C₁₆ and the two constituents of biodiesel, i.e. C₁₆ and C₁₈ fatty acid methyl esters (FAME), did not coelute with any aliphatic hydrocarbons. The analytical curve is presented in Figure 5. The regression coefficient (*r*²) of

0.989 was more than suitable for the quantitation of HVO of 1% to 90% (v/v) in diesel/biodiesel blends. Further evidence of adequate calibration was the random distribution of the residues. Noteworthy, the root mean square error of calibration (RMSEC) was 3.2% (v/v) for the broad analytical curve, 1% to 100% (v/v), but a RMSEC value of 1.5% (v/v) may be attained using a narrower analytical curve from 1% to 25% (v/v).

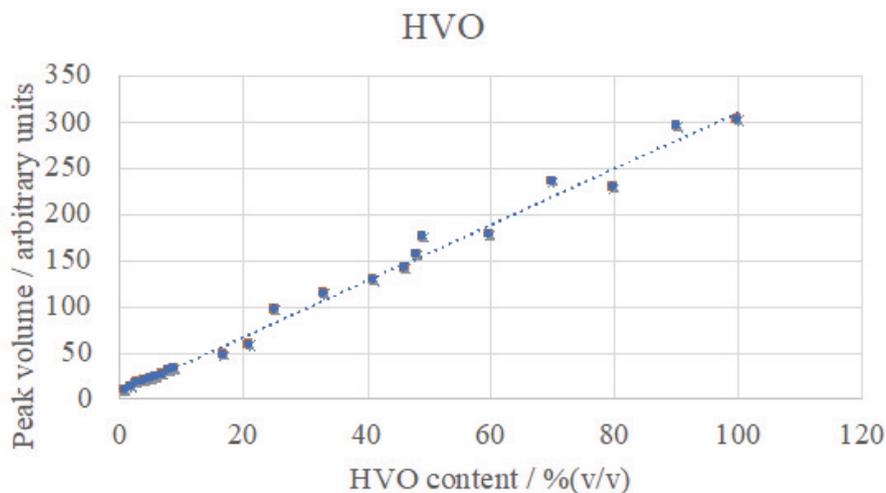


Figure 5. Proof-of-concept analytical curve attained for the quantitation of hidroprocessed vegetable oil (HVO) in HVO/diesel/biodiesel blends. Regression coefficient: $r^2 = 0.989$.

CONCLUSIONS

Flow switching modulation is an excellent alternative for QA/QC of fuels, including hidroprocessed vegetable oil, diesel, and biodiesel, as it provides enhanced peak capacity and fast chromatographic analysis. Furthermore, low-duty cycle and full transfer flow modulators are expected to speed the adoption of GC×GC methods for routine analysis as it offers expectational chromatographic performance and selectivity without increasing the cost of the analysis.

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