ARTICLE IN PRESS

Catalysis Today xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Comprehensive GC × GC chromatography for the characterization of sulfur compound in fuels: A review

Chantal Lorentz[a], Dorothée Laurenti[a], José Luiz Zotin[b], Christophe Geantet[a,*]

[a] *Institut de recherches sur la catalyse et l'environnement de Lyon, IRCELYON, UMR 5256 CNRS—Université Lyon 1, 2 Avenue Albert Einstein, F-69626 Villeurbanne, France*

[b] *PETROBRAS S.A.— R & D Center (CENPES), Av. Horácio Macedo, 950, Cidade Universitária, Rio de Janeiro, RJ 21941-915, Brazil*

ARTICLE INFO

Keywords:
Comprehensive GC × GC
Fuels
Sulfide compounds
S detectors

ABSTRACT

Since the beginning of the 2000's, comprehensive GC × GC chromatography brought a totally new way to characterize complex matrices. This disruptive technique is well adapted to fuels and rapidly gained importance in R & D laboratories of oil (and related) companies. Therefore, this analytical tool has been applied to many aspects of refining and especially the challenge of reducing the sulfur content in fuels. The present article reviews the use of comprehensive GC × GC for understanding the nature of sulfur compounds in refinery products (from gasoline to VGO) and their catalytic conversion through various catalytic processes such as HDS, AOTS, ODS. Various types of detectors (universal or specific) as well as HT GC × GC have been applied and can be combined in order to get a better description of the S compounds in oil products.

1. Introduction

Natural world is providing to chemists complex mixtures such as petroleum which contains 105–106 components. Therefore, the understanding of the properties and reactivity of petroleum oils fractions is highly depending on the accuracy of separation methods mostly based in chromatography. In fact, the rapid growth of chromatography is based on the strong need of petroleum based industries for suitable tools. The introduction in the 90's by Phillips [1,2] of comprehensive two-dimensional gas chromatography (GC × GC) brought a new technique especially suited for the analyses of petroleum feeds and products, which have been the first types of samples used to test these new instruments. In the early 2000's refiners (ExxonMobil, Shell, ENI) and related companies (IFPEN UOP) developed this technique in their research centers which is now used as a routine one in industrial laboratories [3]. Petroleum cuts contain mainly hydrocarbons but impurities such as S N and metals (V Ni Si) contribute even at low concentrations to poisoning deactivation and pollution and thus their removal is required. The main forms of S compounds in light petroleum fractions are mercaptans and polycyclic aromatic sulfur heterocyles. Since the 90's the introduction of more stringent legislation on sulfur compounds in fuels the so-called "sulfur challenge", now requires less than 10 ppm of S in fuels in the most developed countries (or even lower S content if Fuel Cells applications are considered). In such way, hydrodesulfurization (HDS) has become a major process in refineries [4]. The improvement of the process focused the attention in the 90's on the refractory compounds contained in gas oils. They were mainly identified by 1D chromatography associated with a specific S detector (mostly SCD). Alternative processes for desulfurization, such as Olefin Alkylation of Thiophenic Sulfur (OATS), oxidative desulfurization (ODS) and reactive adsorption process (S Zorb) were also investigated in order to improve the efficiency of desulfurization [5]. Furthermore the growing demand of high value petroleum products such as middle distillates gasoline and jet fuels has also pushed refiners to converts the heaviest fractions and extra heavy crude oils which contains even higher content of heteroatoms organo-compounds. Therefore the improvement of catalytic processes is drastically linked to a better knowledge in the composition of the feeds and their products after processing. Comprehensive GC × GC is one of the major analytical tools which can face up these challenges by exploring both compositions and reactivity of S organic compounds in a complex hydrocarbon matrix even if present in low concentrations (ppm level). The purpose of the present review article is to illustrate the strong benefit provided by comprehensive GC × GC in the understanding of refining processes

---

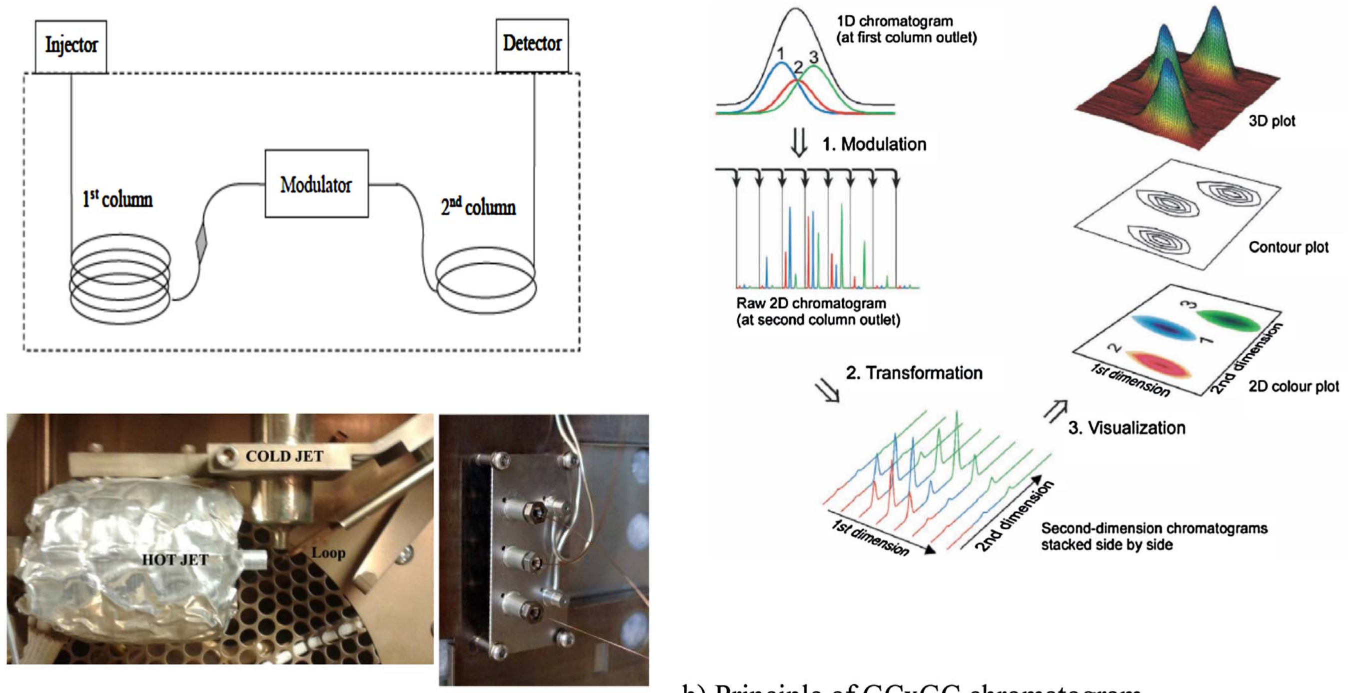
Abbreviations: AED, atomic emission detector; CFT, capillary flow modulator; FCC, fluid catalytic cracking; FID, flame ionization detector; FPD, flame photometric detector; GC×GC, comprehensive gas chromatography; HT GC × GC, high temperature comprehensive gas chromatography; HGO, heavy Gas Oil; LCO, light cycle oil; ODS, oxidative desulfurization; OATS, olefin alkylation of thiophenic sulfur; PFPD, pulsed flame photometric detector; q-MS, quadrupole mass spectrometer; SCD, sulfur chemiluminescence detector; SRGO, straight run gas oil; TOF-MS, time of flight mass spectrometry; VGO, vacuum gas oil

[*] Corresponding author.

E-mail address: christophe.geantet@ircelyon.univ-lyon1.fr (C. Geantet).

http://dx.doi.org/10.1016/j.cattod.2017.04.052
Received 3 February 2017; Received in revised form 21 April 2017; Accepted 24 April 2017
0920-5861/

Please cite this article as: Lorentz, C., Catalysis Today (2017), http://dx.doi.org/10.1016/j.cattod.2017.04.052



b) Principle of GCxGC chromatogram.

a) Configuration of GCXGC and modulators

Fig. 1. Principle of comprehensive GCxGC: a) configuration of columns and modulator and images cryogenic and flow modulators, b) role of modulation and 2D image reconstruction method (from ref [7]).

Table 1
GCxGC detectors used for characterizing S compounds in petroleum liquids.

Detectors	Specificity	Frequency (Hz)	Application	Reference
FID	C—C and C—H bonds, requires analytes	100	Heavy Cat. Cracked Cycle Oil	J. B. Phillips and J. Beens [2]
SCD	S compounds	50	Middle distillate	Ruiz Guerrero et al. [14]
			“	Hua et al. [15]
			“	Wang et al. [16]
			“	Blomberg et al. [17]
			“	Vendeuvre et al. [18]
			“	Choudhary et al. [19]
			SRGO (ODS)	Adam et al. [20]
			Jet Fuel (ODS)	Timko et al. [21]
			VGO	Mahé et al. [22]
			Crude oil	Hua et al. [23]
			Shale oil	Blomberg et al. [17]
				Dijkmans et al. [24]
FPD	S compounds	100	SRGO, kerosene	Toussaint et al. [25]
			Gasoline (OATS)	Chin et al. [26]
				Obame et al. [27]
AED	Multi element	10	FCC	van Stee [28]
q- MS	Mass spectroscopy	30	SRGO	Toussaint et al. [25]
	0–200 m/z		Gasoline	Obame et al. [27]
TOF- MS	Mass spectroscopy	100	Cracked cycle oil	Van Deursen et al. [29]
	Total scan		HGO	Dallüge et al. [7]
				Machado et al. [30]
				Timko et al. [21]

for S removal.

2. Principles of GC × GC technique

GC × GC technique has a heart cutting nature (connection in series of two chromatographic columns) and is based on the introduction of a “so called” modulator between two chromatographic columns (see Fig. 1a) [6]. A few small fraction of the first dimension column elutes in the second column for further separation as it was well illustrated by Dalluge et al. (Fig. 1b) [7]. Thus, the overall peak capacity is the product of the peak capacity of the two columns providing an outstanding resolution. However, to prevent overlapping in the information the second columns is a short one, typically close to one meter. The combination of non polar/polar columns brings also the advantage of orthogonality as defined by J. C. Giddings [8]. It evidences ordered distributions of family products as illustrated by Marriott et al. [9], with alignment of peaks (blobs) corresponding to a step by step increase of methyl groups in the parent molecule, so called “roof tile effect”.