Catalysis Today 143 (2009) 172–178

Contents lists available at ScienceDirect

Catalysis Today

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

Co-processing of pyrolisis bio oils and gas oil for new generation of bio-fuels: Hydrodeoxygenation of guaïacol and SRGO mixed feed

Van Ngoc Bui, Guy Toussaint, Dorothée Laurenti, Claude Mirodatos, Christophe Geantet *

Institut de Recherches sur la Catalyse et l'Environnement (IRCELYON), UMR5256 CNRS Université Lyon 1, 2 Av. A. Einstein, F-69626 Villeurbanne, France

ARTICLE INFO

Article history:
Available online 20 January 2009

Keywords:
Guaiacol HDO
Co-processing hydrotreating
2D-GC–MS

ABSTRACT

Within the frame of second generation bio-fuels development, the present work reports for the first time the impact of co-processing guaiacol as an oxygenated molecule representative of pyrolitic bio oils with a straight run gas oil (SRGO) in the framework of a hydrodesulfurization process (HDS). The reaction scheme observed during the hydrotreating of the sole guaiacol in the gas phase was compared to the conversion products observed during the co-processing of guaiacol with the SRGO, by using the two dimensional GC–MS analysis. During the co-processing, a decrease of the HDS performance of a reference $CoMo/Al_2O_3$ catalyst was observed at low temperature and high contact time. It was assigned to the formation of intermediate phenols competing with sulfur containing molecules for adsorbing on hydrogenation/hydrogenolysis sites. Above 320 °C, complete hydrodeoxygenation (HDO) of guaiacol was observed and HDS could proceed without any further inhibition.

1. Introduction

Significant quantities of biomass are available from wood industries, residues of pulp and paper manufacture, fermentation by-products and other forestry residues. After conversion by fast pyrolysis and subsequent appropriate upgrading into liquids often named "bio oil" [1–3], these feedstocks can act as crude oil substitute in conventional refinery units and thus afford significant CO_2 emission abatement based on a seed-to-wheel analysis. The possibility to co-process these bio oils in various refining units may lead to second generation bio-fuels, meeting the present and future EC regulations. Implementing these co-processing techniques in petroleum refineries can result in a competitive advantage for both refiners and society at large. First of all, they involve alternative feeds that are renewable and potentially cheaper than mineral oil. Secondly, they can reduce the costs of producing fuels and chemicals from bio-feeds by utilizing the existing production and distribution systems for petroleum-based products and avoiding the establishment of parallel systems. Last, but not least, they provide a base production for fuels and chemicals that is less threatened by changes in government policies toward fossil feeds and renewables. In order to investigate this kind of co-processing, the BIOCOUP project [4], supported by the European Commission through the Sixth Framework Program for Research and Technological Development, intents to develop a chain of process steps, which would allow bio oils feedstock to be co-processed in standard refinery units. The present work illustrates this impact study for the case of hydrotreating (hydrodesulfurization or HDS) units. The use of renewable feedstock in a conventional HDS unit should not modify the quality of the products which must follow the drastic legislation on S content (10 ppm of S in 2009 according to EC regulations [5]). The average composition of raw pyrolisis oil is 50–65% of organic components, 15–30% of water and 20% of colloidal lignin fraction. More than 400 different organic components have been detected which can be classified in several groups: organic acids, aldehydes, ketones, furans, phenolic compounds, guaiacols (methoxyphenols), seryngols and sugar-based compounds [6–8]. Under hydrotreating conditions, oxygenated compounds will mostly react through hydrodeoxygenation (HDO) route which means C–O bonds cleavage and production of water. Among these O-containing compounds, the highly representative guaiacol molecule (2-methoxyphenol) presents the interest to possess two different oxygenated functions (phenolic and methoxy group), the first one being considered as the most difficult C–O bond to cleave [9]. Thus, this molecule has been used as a probe molecule in the early studies on hydrodeoxygenation [10,11]. Several reaction schemes were proposed and intermediates have been identified. In the present work, we will attempt first to describe in detail the different

---

* Corresponding author. Tel.: +33 4 72 44 53 36; fax: +33 4 72 44 53 99.
E-mail address: christophe.geantet@ircelyon.univ-lyon1.fr (C. Geantet).

0920-5861/$ – see front matter © 2009 Published by Elsevier B.V.
doi:10.1016/j.cattod.2008.11.024

conversion pathways of guaiacol under HDO conditions. Then, we will illustrate the co-processing of this model compound with a straight run gas oil (SRGO).

As stressed above, the limit in sulfur content is one of the most drastic parameters that must meet the refiners [5]. While in refineries, HDS aims at reach this target, co-processing with oxygenated molecules will also involve HDO reactions which also consume hydrogen and might compete with HDS. Far that reason, the impact of adding guaiacol under various HDT conditions has to be studied by investigating the reaction mechanism of this single molecule in the complex matrix of the SRGO. For unraveling this mechanism, the sophisticated two-dimensional chromatography coupled with mass spectrometry (2D GC–MS) analysis has been used as a recent technique which is becoming a standard in the refining industry due to its important peak identification capacity [12–14].

2. Experimental

2.1. Catalytic testing of guaiacol in gas phase

Guaiacol hydrotreatment was performed on a reference commercial CoMo/Al_2O_3 catalyst provided by Shell Global Solutions Int. B.V.

The catalytic tests were first carried out in a fixed bed tubular reactor [15] equipped with a pyrex reactor inserted into a stainless steel one. The reaction temperature was 300 °C, the total pressure 4 MPa; guaiacol was introduced by means of a saturator/condensor system at a partial pressure of 2.67×10^3 Pa, and hydrogen sulfide (H_2S) was added to reach a partial pressure of 100 ppm to maintain the catalyst in a sulfided state during HDO reaction. Catalytic activities were measured at steady state after 12 h on stream. The products were analyzed online by gas chromatography (HP 5890) equipped with a flame ionization detector (FID) with a CP-Sil5 capillary column (length 50 m, i.d. 0.32 mm, film 5 μm). Gas chromatography was controlled by Peak Simple software and analyses were performed automatically every hour. The condensed products were also analyzed by GC–MS (GC HP6890 coupling with MS HP5973) and the product identification was confirmed by manual injection of pure compounds, if available, on GC. Response factors were determined experimentally using pure compounds and they served as a basis for the determination of the molar balance. The catalyst was activated ex situ under a flow of H_2S/H_2 15% (v/v) at 400 °C for 4 h (rate 10 °C/min, flow rate 4 L/h). At the end of sulfidation, the catalyst was cooled down under nitrogen flow and stored under argon to avoid oxidizing by air contact.

2.1.1. Catalytic testing of guaiacol with a SRGO

Catalytic hydrotreatment tests were performed in a trickle bed reactor described in [16,17]. The feed was a SRGO (S content 13,500 ppm) crude or spiked with 5000 ppm of guaiacol. The reactions were performed between 280 and 360 °C, with two LHSV (LHSV: liquid hourly space velocity) 1 or 2 h^{-1}, and a total pressure of 4 MPa with liquid flow and gas flow (H_2) of respectively 2 g/h–15 ml/min or 4 g/h–30 ml/min. 1.5 g of grounded sulfided CoMo/Al_2O_3 catalyst (sieved between 100 and 600 μm) were placed between two layers of alumina in an up-flow tubular reactor (4 cm^3). A periodic sampling of the liquid effluent was performed and the total sulfur content was determined. Activation of the catalysts was performed on line with a H_2/H_2S 95/5 gas mixture at 400 °C for 2 h at atmospheric pressure (20 ml/min).

2.2. Catalyst characterization and reaction effluent analysis

2.2.1. Total sulfur analysis

Total sulfur analysis was performed on an elemental analyzer ANTEK 9000NS. After a complete high temperature oxidation of the entire sample, the SO_2 formed is exposed to UV radiation. The fluorescent emission is specific for sulfur and allows quantifying it. Crude oil and HDS samples were diluted 10 times.

2.2.2. Two dimensional GC–MS

The GC × GC system was installed in a modified 6890N gas chromatograph (Agilent) equipped with a two stages thermal modulator (Zoex Corporation). A single low temperature valve mounted outside the GC oven controls the cold jet ($-100\,^{\circ}C < T < -120\,^{\circ}C$) which provides narrow chemical pulses. A short thermal desorption (280 °C) releases the trapped solutes and achieves the injection in the second column. The modulator accumulates samples eluting from the first column for a period equal to one third to one fifth of the duration of an individual peak. Typically, a modulation period of 12 s was used. The secondary column effluent was analyzed using a mass selective detector 5975B (Agilent), with an acquisition of 22 scans/s in the mass range of 45–300 UMA. In principle, the linearity of MS detector allows to calculate, using a linear regression, the concentration of each detected compounds, if the pure compounds are available for calibration. In this work, we only mention the total response of the MS detector as an indication of the evolution of specific compounds; thus providing a semiquantitative analysis.

The carrier gas was high purity helium regulated at a constant flow of 1.2 ml/min (initial pressure 36 psi). The temperature of the first GC column was programmed from 50 °C (5 min hold) to 300 °C (5 min hold) at a rate of 1.5 °C/min, the temperature of the second was from 50 °C (hold 5 min) to 325 °C (18 min hold) at 1.8 °C/min.

Fuel samples were injected undiluted with a 1 micro-syringe (0.4 μl) and a split ratio of 250. The first column used was a 30 m, 0.25 mm i.d., 0.2 μm film thickness DB5 MS Agilent, the second column was a 1.2 m, 0.1 mm i.d., 0.2 μm film thickness VH 17 MS Varian. The two columns were connected with a standard union, thus the second column worked under Fast GC conditions. Molecules were separated on the basis of independent chemical properties: volatility for the first column and polarity for the second.

The raw signal (total ion count) of a GC × GC experiment is a time ordered series of second dimension chromatograms. The data analysis (GC Image Zoex Corporation) constructs a two dimension chromatogram by placing the second chromatograms side by side. The software GC Image [18] also constructs a 3D image by placing the detector response on the third axis. In GC, the concentration of a compound is related to the area of the corresponding peak; in GC × GC the concentration is related to a volume so called a blob. When GC peaks are identified using their retention times, GC Image uses a template pattern matching to automatically identify and characterize peaks of interest in runs of similar samples under similar conditions. Each sample output is associated with a value representing the volume, and with a mass spectrum consisting of an array of mass/z-intensity pairs. The mass spectra can be used to identify unknown chemicals. Linear alkanes of the SRGO were considered as reference compounds to check repeatability of the injection and quantification of peak volumes. This variation from injection to injection is in the range of 2% preventing the use of an internal standard for quantification.

As an image processing facility, polygons or rectangles can be drawn to indicate a set of volumes whose peaks are contained in the graphic and which satisfy rule-based constraints on set inclusion. These rules deal with the retention time, the presence of mass fragments or an arithmetic relation between mass/*z* and intensity as extracted from mass spectra.

3. Results and discussion

3.1. Guaiacol conversion under HDO conditions

Preliminary experiments on the HDO of guaiacol were performed in order to get a complete overview of the reaction scheme. From the early studies on guaiacol conversion [10], the basic reaction scheme proposed involved consecutive transformations into catechol, phenol intermediates and HDO compounds (benzene, cyclohexane). Methylated compounds, heavier compounds and coking [19] were mentioned. Starting from guaiacol, the removal of the methoxy group may involve two reaction routes. The first one is demethylation (DME) which gives CH_4 as a sub-product and the other one demethoxylation (DMO) which gives methanol. This was evidenced by Centeno et al. [20] while support and doping effects were investigated. As soon as phenol-like molecules are formed, two different pathways may also exist for C–O bond breaking as proposed in the early 1980s [21]. The first pathway entails the direct hydrogenolysis of the C–O bond between the aromatic carbon and the OH group (so called DDO by analogy with direct desulfurization (DDS) route in hydrodesulfurization of DBTs), the second pathway, named HYD, requires a preliminary hydrogenation of the aromatic ring before elimination of the OH groups.

Fig. 1 reports the partial conversion into various products as a function of the total conversion of guaiacol, which reflects well the above-mentioned mechanisms. Thus we can notice that catechol and phenol are formed as primary products. Methylation of the aromatic ring occurred with the formation of tetra- and hexa-methylbenzene, mono- to tetra-methylphenols and dimethyl-catechols (Scheme 1). Heavier products (issued from the condensation of two rings) are also observed in small quantities corresponding to cyclohexylphenol or methylated analogs. Note that the support itself was found not to be inert towards the transformation of guaiacol into catechol or phenol. Under the prevailing reaction conditions, 15% of guaiacol conversion was observed with the alumina support alone (mostly into catechol).

The evolution and nature of HDO products, grouped together in Fig. 1, are detailed in Fig. 2. Products coming from DDO and HYD routes are observed as well as those resulting from the same routes by the transformation of methyl-phenols. Concerning DME and DMO, methane is the main light product of the reaction but methanol is also observed (1/4 of methanol and 3/4 of methane at about 30% of total conversion). From these results, a simplified reaction scheme can be proposed (Scheme 2) which explains the production of the main identified products observed upon guaiacol conversion at 300 °C under 4 MPa of H_2 through different pathways. This simplified scheme does not include the heavier products described above and methylated compounds presented are restricted, in that scheme, to monomethylation but should include in fact dimethyl and trimethyl compounds which are also observed.

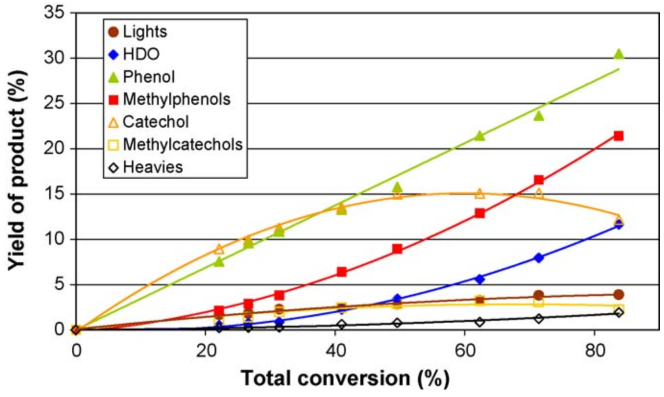
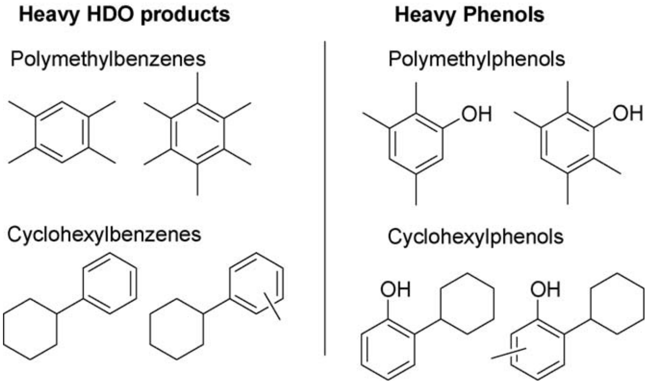


Fig. 1. Distribution of products versus conversion of guaiacol on a CoMo on alumina sulfide catalyst at 300 °C, 4 MPa and 100 ppm of H_2S.



Scheme 1. Heavy products of guaiacol conversion identified by GC–MS.

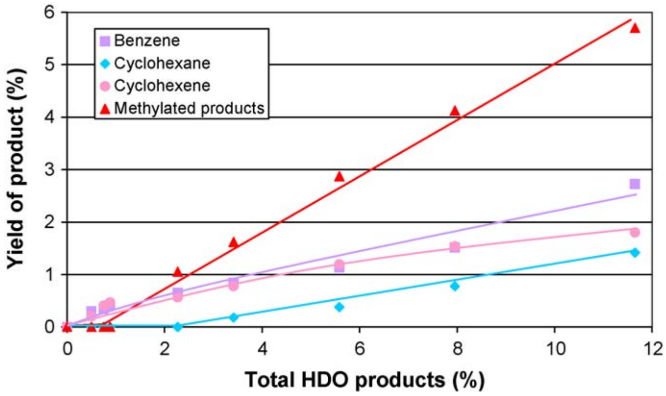


Fig. 2. Distribution of HDO products versus HDO conversion of guaiacol on a CoMo on alumina sulfide catalyst at 573 K, 4 MPa and 100 ppm of H_2S.

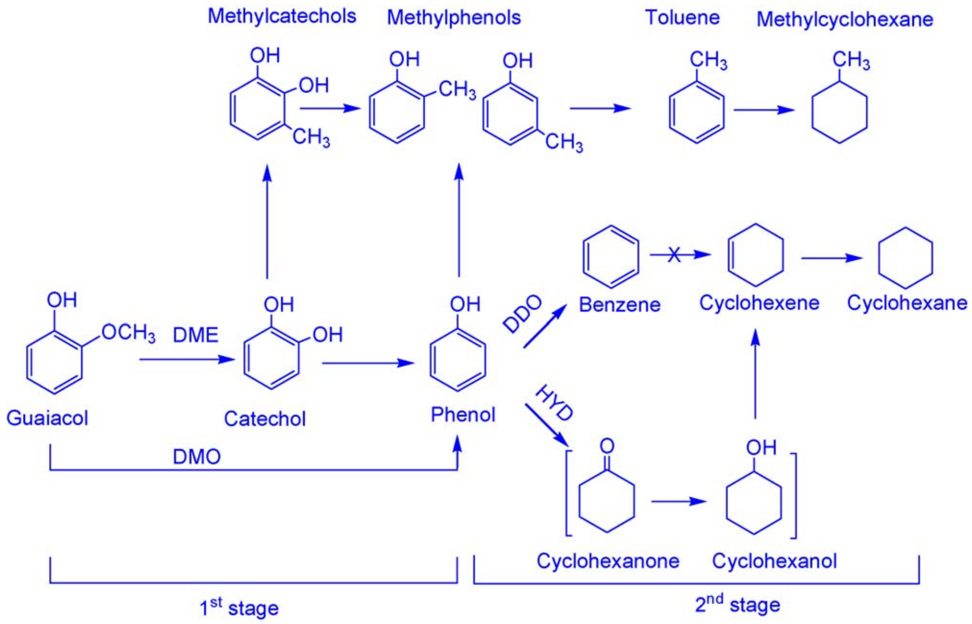
3.2. Co-processing of guaiacol and SRGO

Preliminary experiments of co-processing a SRGO, containing 13,500 ppm of S, with 5000 ppm of guaiacol were performed at a LHSV 1 h^{-1} and in the temperature range of 320–360 °C. Under these conditions no significant effect was observed on the extent of hydrodesulfurization. Thus, it was decided to investigate the conversion at shorter contact time (LHSV 2 h^{-1}) and lower temperature.

The detailed conversion of the oxygenated compound within the complex matrix of the SRGO was followed using 2D GC–MS chromatography. The 2D chromatogram of the SRGO feed is reported in Fig. 3. Due to the combination of two different columns, a clear description of the feed is obtained and all the compounds are grouped in several families (alkanes, mono-, di-, tri-aromatics).

When 5000 ppm of guaiacol was added to the feed a well-identified contribution appeared in the 2D chromatogram. A zoom of the region of interest (Fig. 4) shows that the polarity of guaiacol enables a perfect separation of this compound even within the complex matrix of the SRGO feed.

Global GC analysis (Fig. 5) of the sample collected after conversion at 280 °C shows that new products like phenol, methylphenols, toluene, cyclohexene, cyclohexane and benzene appeared, which were not observed in the SRGO conversion alone, and therefore could be ascribed to guaiacol conversion. These specific products were thus analyzed by 2D GC–MS after hydrotreatment at different reaction temperatures. The light



Scheme 2. Reaction pathways for the conversion of guaiacol at 573 K under 4 MPa of H_2 on a CoMo on alumina sulfide catalyst.

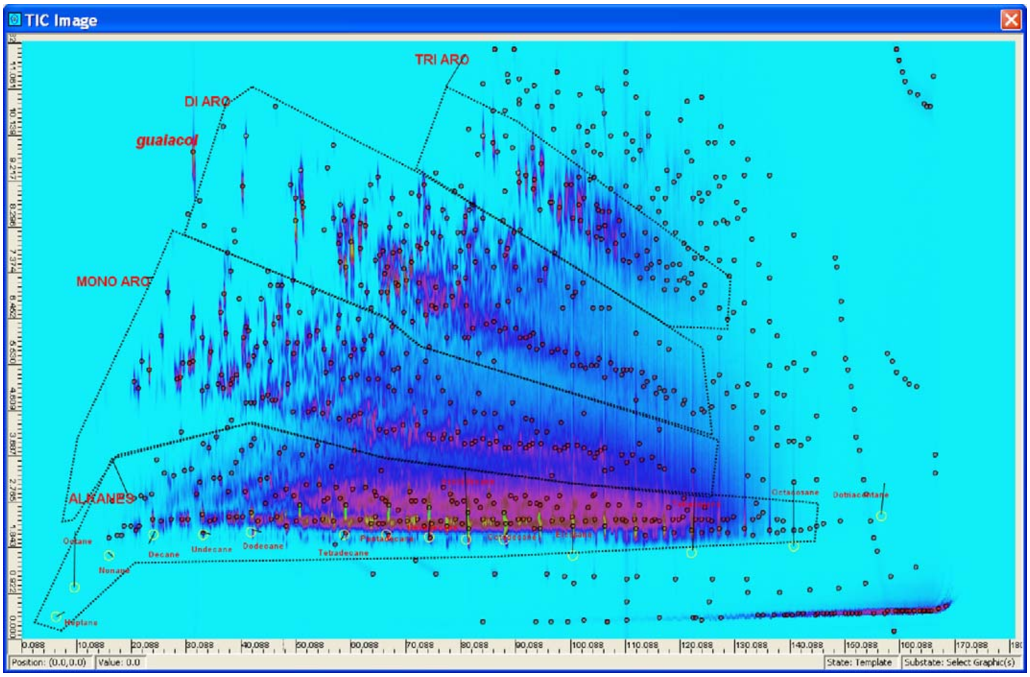
products region is zoomed in Fig. 6 after conversion at 300 °C. The presence of methylated compounds such as methylcyclohexane could be noted as well.

From the 2D chromatograms and the volume of the 3D peaks, it was possible to quantify the contribution and the evolution of these by-products; naphthalene conversion was also evaluated as a characteristic compound of our reference SRGO.

Fig. 7 illustrates how the amounts of intermediate phenolic compounds formed from guaiacol (and present at the lowest temperatures) decrease with reaction temperature as well as the MS response of naphthalene into the hydrogenated products. Methylation reactions occurred, like in the case of pure guaiacol conversion, introducing new by-products in the reaction scheme.

The formation of the hydrocarbons, i.e. toluene, xylenes, cyclohexene, benzene, and cyclohexane produced from guaiacol HDO as a function of temperature is depicted in Fig. 8. As can be seen, the formation of each compound coincides with the disappearance of the phenolic compounds, as expected from Scheme 2.

Let's consider now the impact of the presence of guiaiacol on HDS conversion. This impact of guaiacol addition to the feed is illustrated in Fig. 9. As can be seen, an inhibition of the



Position: (0.0,0.0) Value: 0.0 State: Template Substate: Select Graphic(s)

Fig. 3. 2D GC–MS chromatogram of SRGO feed +0.5% of guaiacol before treatment.

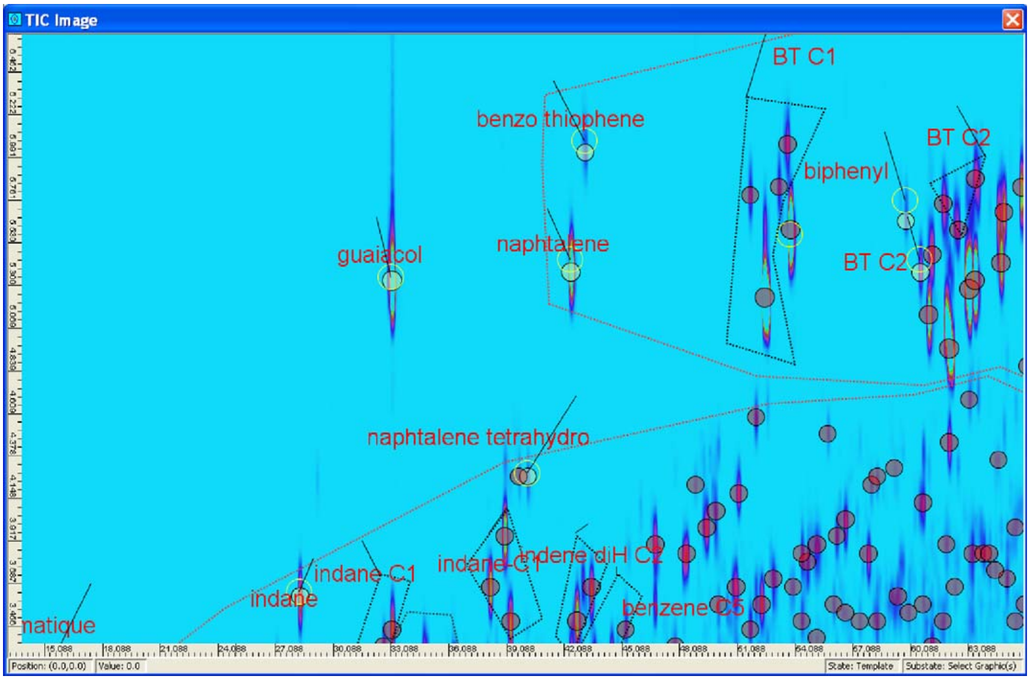


Fig. 4. Zoom on the region of interest for guaiacol conversion products.

desulfurization reaction occurred under these short contact time conditions, which slowly disappeared when the temperature of the reaction was increased. When the reaction is carried out at relatively low temperature (up to about 320 °C) guaiacol is preferentially converted into phenols while the conversion of S compounds appears inhibited, most probably through a competitive adsorption mechanism. An ordering of reactivity of SNO-compounds was already proposed in the late 70's when upgrading of shale oils and coal oils was under investigation [22]. Further competitive reactions on CoMoS/Al_2O_3 type catalysts established the following rank of reactivity: benzothiophene > dibenzothiophene > m-cresol and evidences the competition between HDO and HDS reactions, both reactions exhibiting close apparent activation energies [21]. Until phenol-like compounds remain in the feed, they compete with the most reactive S compounds and inhibit the desulfurization. As soon as the temperature is high enough to convert these phenolic compounds into deoxygenated compounds (i.e. higher than 320 °C),

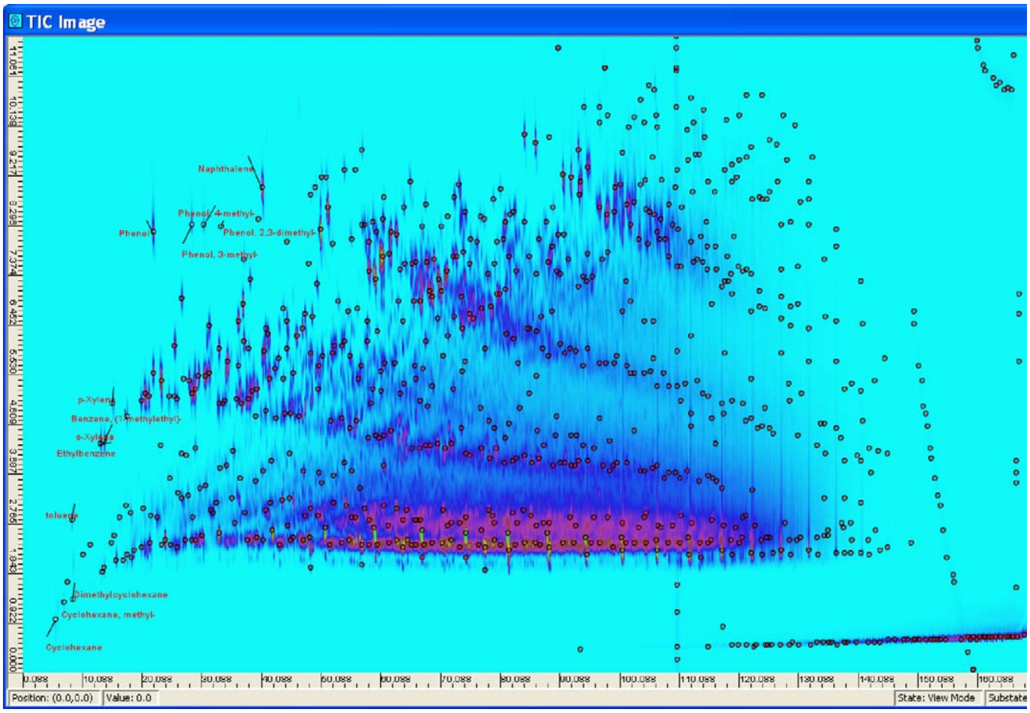


Fig. 5. Global analysis of SRGO + 0.5% of guaiacol after conversion at 280 °C.

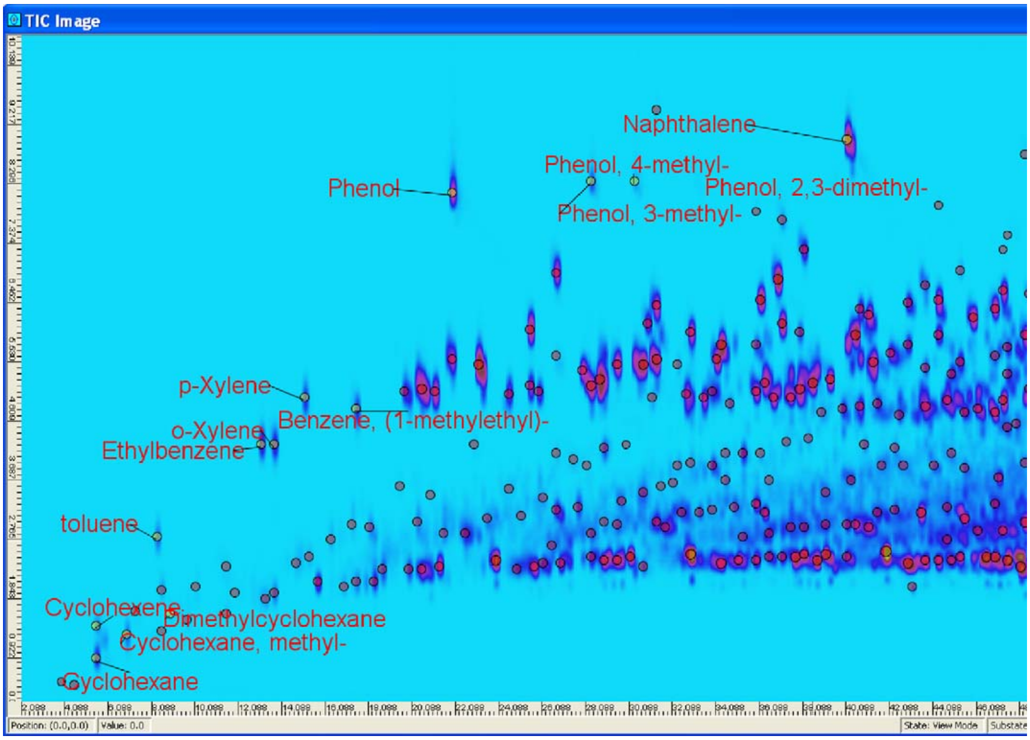


Fig. 6. 2D GC zoom on the volatile region after conversion at 300 °C.

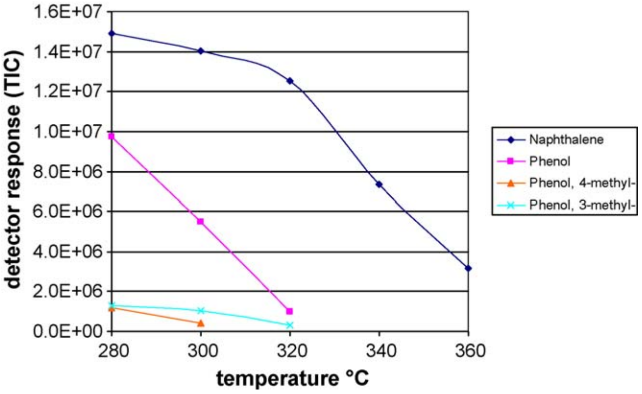


Fig. 7. Changes in the amount (corresponding to total ionic current of the MS) of phenolic compounds and naphthalene during HDS/HDO co-processing as a function of reaction temperature.

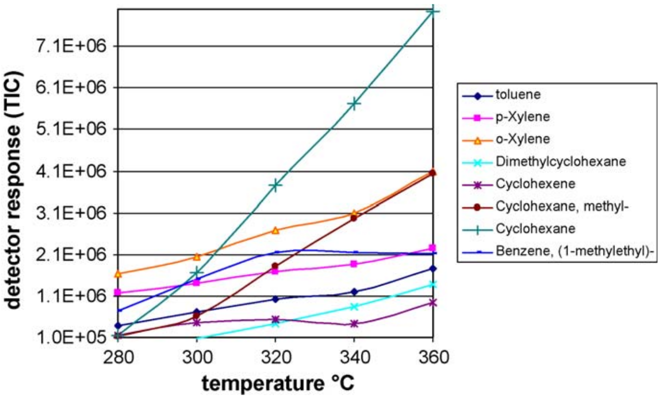


Fig. 8. Variation in the amount (corresponding to total ionic current of the MS) of HDO products of guaiacol during HDS/HDO co-processing as a function of reaction temperature.

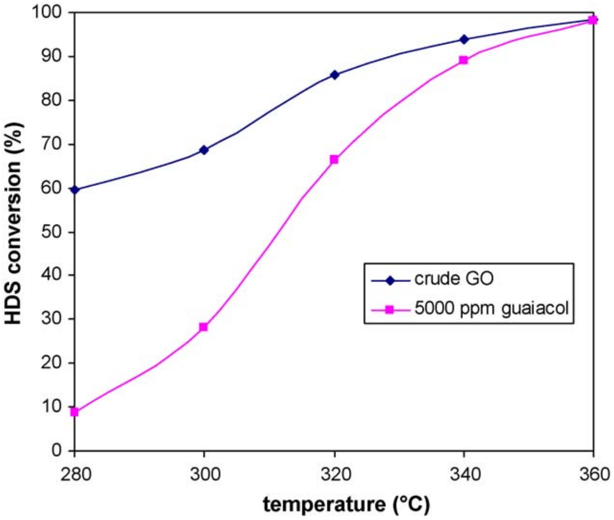


Fig. 9. HDS conversion of SRGO and SRGO + guaiacol versus temperature.

only the most refractory sulfur compounds (4,6-DMDBT type compounds) remained in the product like in the case of deep HDS and no more inhibition effect was observed.

4. Conclusion

In the present work it was attempted for the first time to evaluate the impact of adding guaiacol as a representative molecule of pyrolysis oils to SRGO in a conventional hydrotreating process. As a matter of fact, though this oxygenated probe molecule was subject to many academic studies by itself, its co-processing with SRGO was never reported so far. To that purpose, the reactivity of guaiacol was evaluated either as a pure feedstock in the gas phase or in a trickle bed reactor as an additive to SRGO on a reference sulfided CoMo/Al_2O_3 catalyst.

From the gas phase experiments carried out with only the probe molecule, a reaction scheme was proposed which describes the various routes leading to hydrocarbon compounds via intermediate oxygenates formation. In the presence of SRGO and under deep desulfurization conditions, no inhibiting effect on HDS activity was observed due to guaiacol conversion. However, at mild reaction temperature (below 320 °C) and at reduced space velocity, an inhibition of HDS was observed, likely due to a strong and competitive adsorption of intermediate phenols on the catalyst active sites. By increasing the temperature, these phenolic compounds are rapidly hydrodeoxygenated and the resulting hydrocarbons appear not to compete with HDS reactions.

From a technical view point, 2D GC–MS chromatography allowed us to characterize and to follow the products of guaiacol conversion even within the complex gas oil matrix. Thus, it brought unambiguous evidence that the same intermediate compounds were formed either in the presence (trickle bed reactor) or in the absence (gas phase reactor) of SRGO.

Acknowledgements

Part of this work was funded by the FP6 “BIOCOUP” project and B.V.N. is grateful to CNRS for a grant.

Colin Schaverien (Shell Global Solutions Int. B.V.) is warmly acknowledged for fruitful discussions and SRA instruments for technical help in the development of the 2D GC–MS analysis.

References

[1] T. Bridgwater, Biomass Bioenergy 31 (2007) VII–VII10.
[2] M.F. Demirbas, M. Balat, J. Sci. Ind. Res. 66 (2007) 797–804.
[3] D. Mosham, C.U. Pittamnn, H.S. Steele, Energy Fuels 20 (2006) 848.
[4] http://www.biocoup.eu/.
[5] Directive 2003/30/EC of the European Parliament and of the Council, 2003.
[6] A. Fullena, J.A. Contreras, R.C. Striebich, S.S. Sidhu, J. Anal. Appl. Pyrol. 74 (2005) 315.
[7] J.H. Marsman, J. Wildschut, F. Mahfud, H.J. Heeres, J. Chromatogr. A 1150 (2007) 21.
[8] J.H. Marsman, J. Wildschut, P. Evers, S. de Koning, H.J. Heeres, J. Chromatogr. A 1188 (2008) 17.
[9] E. Furimsky, Catal. Rev. Sci. Eng. 25 (1983) 421–458.
[10] J.B.-s. Bredenberg, M. Huuska, P. Toropainen, J. Catal. 120 (1989) 401–408.
[11] A. Vuori, A. Helenius, J.B.-S. Bredenberg, Appl. Catal. 52 (1989) 41–56.
[12] J. Dallüge, J. Beens, U.A.Th. Brinkman, J. Chromatogr. A 1000 (2003) 69.
[13] R. Edam, J. Blomberg, H.-G. Janssen, P.J. Shoenmakers, J. Chromatogr. A 1086 (2005) 12–20.
[14] C. Vendeuvre, R. Ruiz-Guerrero, F. Bertoncini, L. Duval, D. Thiebaut, Oil Gas Sci. Technol. 62 (2007) 43–55.
[15] M.L. Vrinat, L. de Mourgues, React. Kinet. Catal. Lett. 14 (1980) 389.
[16] D. Letourneur, M. Vrinat, R. Bacaud, Stud. Surf. Sci. Catal. 106 (1997) 491–497.
[17] D. Letourneur, R. Bacaud, M. Vrinat, D. Schweich, I. Pitault, Ind. Eng. Chem. Res. 37 (1998) 2662.
[18] S.E. Reichenbach, M. Ni, V. Kottapalli, A. Visvanathan, Chemom. Intell. Lab. Syst. 71 (2004) 107.
[19] E. Laurent, B. Delmon, Appl. Catal. 109 (1994) 77–96.
[20] A. Centeno, E. Laurent, B. Delmon, J. Catal. 154 (1995) 288–298.
[21] E.O. Odebunmi, D.F. Ollis, J. Catal. 80 (1983) 56–64.
[22] L.D. Rollman, J. Catal. 46 (1977) 243–252.