SIMULATED DISTILLATION OF HEAVY FRACTION BY CAPILLARY SUPERCRITICAL FLUID CHROMATOGRAPHY. EVALUATION AND COMPARISON WITH GC

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Introduction

Simulated distillation (Simdis) based on gas chromatography (GC) is widely used in the petroleum industry for evaluation of fossil fuels as well as petroleum feeds and cuts treated in refining and conversion processes. Through a calibration curve relating the boiling point of normal paraffins to their elution temperature or retention time, simdis gives the hydrocarbon distribution of the sample (in weight percent) versus the boiling range of the fraction (expressed in Atmospheric Equivalent Boiling Point, AEBP). The conditions used for simdis[1] are tuned to provide results in agreement with preparative distillation that gives the True Boiling Point (TBP) curve (described in ASTM D2892). Several methods have been standardized (ASTM D2887, D5307) for samples with a final boiling point (FBP) up to 538 °C (1000 °F). Much effort has gone into extending the range of eluted compounds and the standardization of a method up to an FBP of 700 °C is in progress (ASTM proposed test method, 1994). However, at oven temperatures up to 430 °C in high-temperature GC, the resistance of high molecular-weight hydrocarbons (HMHs) to cracking reactions is questionable[2,3,4]. This is not the case in supercritical-fluid chromatography (SFC) as high temperatures are not needed and the mechanism for extending the upper limit depends on sample solubility not volatility. Indeed, the main advantage of SFC over GC techniques comes from the solvent strength of the mobile phase. The polarity of the most commonly used supercritical mobile-phase, CO_2, depending on the operating conditions, varies between that of pentane and toluene, making SFC a potentially powerful technique for the elution of HMH at much lower temperatures than GC. This communication presents recent advances in Simdis of heavy fractions using SFC. Compared to GC, SFC calibration range is extended up to C_{120} hydrocarbons and can be extrapolated to nC_{162}, As in GC, using element selective detectors SFC could be the tool of choice for better quantitation of conversion in heavy petroleum-fraction processing.

Experimental

Samples. The samples of feed and effluents of hydrotreatment units were obtained from IFP pilot plants. The so-called feed A is a vacuum residue having the following properties: viscosity (100°C) = 1000 cst; density15/4 = 1.028; % weigh eluted at FBP (D 2887) = 48 %w/w. The effluents were obtained after demetallization (HDM) and after HDM and desulfurization (HDS) unit. Polyethylene standard like Polywax 650 and 1000 were also used to generate retention time versus boiling point calibration.

Characterization Method. An ISCO 100D supercritical fluid syringe pump equipped with specific cooling device was used. The chromatographic column was placed into a HP 6890 gas chromatograph equipped with a flame ionization detector and coupled to G 2350 A atomic emission (Agilent technologies). Splitless injections were done using a Valco Valve CI4WE1 using 1200 nl loop at 120°C after dilution into xylene for dissolving samples[3]. A (5 m x 0.05 mm x 0.2 µm) capillary column DB-5 from JW was used as stationary phase. GC simdis was performed upon the ASTM standard method (ASTM D2887, D5307 and ASTM proposed test method for HT-GC, 1994)[4] for samples with a FBP up to 538 °C and 700 °C, respectively. The SFC system is described in **Figure 1**.

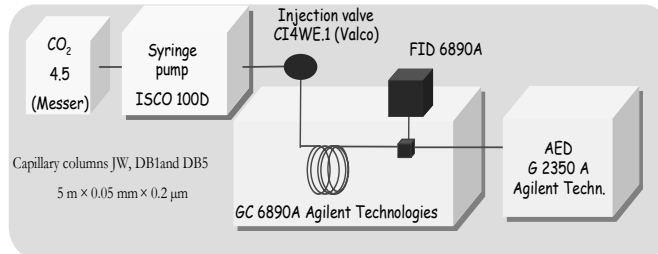

Figure 1. SFC-AED-FID hyphenation

Results and discussion

SFC simdis. Operating conditions (type stationary phase, oven temperature and pressure gradient, injection) were optimized to obtain true relation ship between retention and boiling point and to avoid discrimination of sample during the injection step. Besides, it has been necessary to obtain the lowest difference between the retention of different compounds having the same boiling point (e.g. alkanes and aromatics) for better accuracy of distillation curves. Polydimethylsiloxane bounded phases were carried out to provide no selectivity versus structure[3,5]. Thanks to optimisation of phase ratio, the heaviest compound eluted was n-C_{118}, what was quite higher than previously reported (C_{108})[5]. An example of chromatogram of standard mixture is given on **Figure 2**.

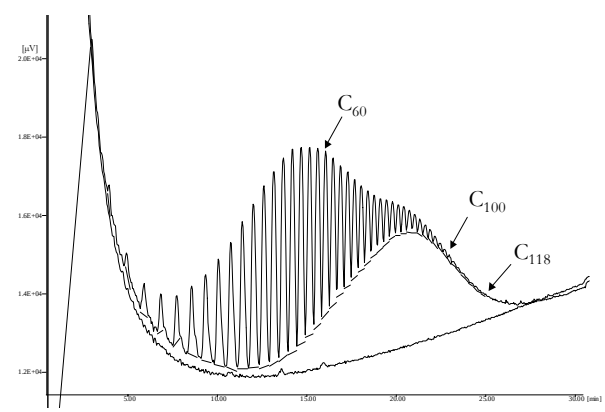

Figure 2. Chromatogram of polywax 655/1000 mixture (50/50 w/w/). Conditions: Column DB5 (5 m × 0,05 mm × 0,2 µm); 6.6 g/L; Flow-rate (CO_2) = 3 ml / min; T_{oven} = 160°C; Pressure (CO_2) 100 bars to 500 bars (30 min) at 13.3 bars/min.

Routine detection of n-C_{120} (750 °C) was observed, what means a benefit of 20 carbons benefit with regard to HT- GC (e.g. end point benefit of 50 °C). Repeatability was daily checked as critical for simdis: 20 injections of a test mixture over 35 days lead to retention time RSD less than 0.3%.

Model of retention vs. number of carbon atoms in SFC. Owing to the lack of resolution, it was not possible to identify elution peaks at the end of the chromatogram of Polywax 1000. In order to calibrate this part of the chromatogram, a model calculating n-paraffins retention times between C_{50} and C_{100} as a function of their

number of carbon atoms has been implemented. This model has been performed to check for retention time of n- paraffins in the range of C_{100} to C_{120}, for whom retention times were known from the chromatogram, and to predict retention times in the range of C_{120} to C_{162}. The comparison between calculated and measured retention times for the identified alkanes over C_{100} lead to a bias lower than 0.07 minute. The extrapolated retention times have been used to generate simulated distillation curves from C_{26} (412 °C) to C_{162} (817 °C). The **Figure 3** shows measured retention times (from C_{26} to C_{118}) and extrapolated retention times (from C_{100} to C_{162})

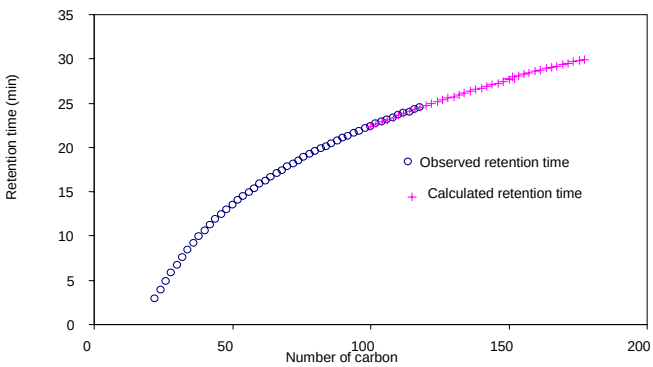

Figure 3. Comparison of extrapolated and measured retention times.

This model was carried out to characterize heavy ends using *extended SFC simdis*.

Application to feed and cuts of hydroconversion units. Our system was carried out to characterize feed A (vacuum residue) for hydroconversion unit. **Figure 4** shows the chromatogram and the upper boiling point limit typically obtained using HT-GC (nC_{106}, 731°C) and extended SFC (nC_{162}, 817°C) are indicated on the chromatogram.

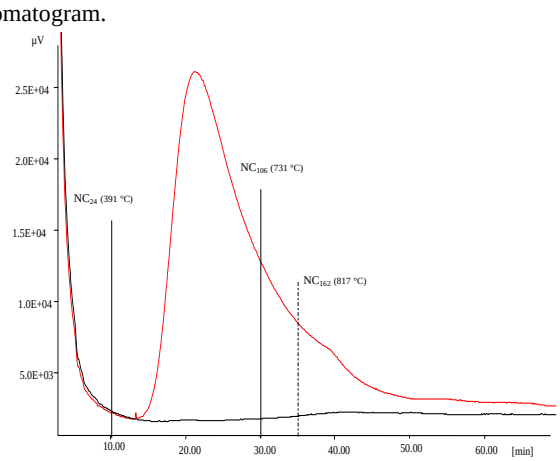

Figure 4. Chromatogram of A feed (vacuum residue)
Conditions: Column DB5 (5 m × 0,05 mm × 0,2 µm); 100 g/L; Flow-rate (CO_2) = 2 ml/min; T_{oven} = 160°C; Pressure (CO_2) 100 bars (5 min) to 550 bars (30 min) at 13.3 bars/min.

Clearly, the ability of SFC to provide the elution of HMW enables a better representation of the feed: the FBP according to HT-GC simdis corresponds to 74 % w/w of eluted fraction using SFC, what is quite less than 85 % w/w of the eluted fraction at FBP using extended SFC simdis. **Figure 5** shows simulated distillation curves obtained for HT-GC, SFC and extended SFC.

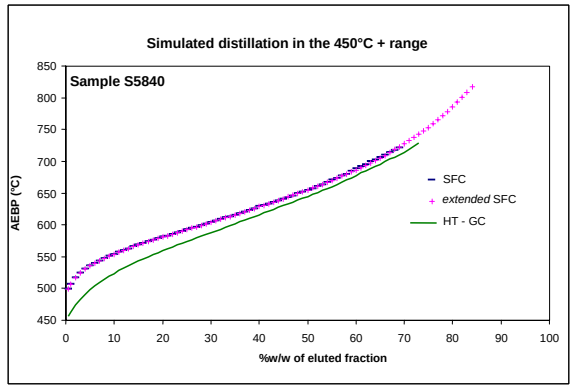

Figure 5. Comparison of simdis curves using HT-GC, SFC and extended SFC.

It is obvious that good agreement is observed between the GC and SFC data in the range of 450 °C to 731°C, as previously reported[3,5]. Using extended SFC, the upper limit can be raised above 810 °C, enabling approximately 90% of this heavy residue to be characterized. **Table 1** reports the weight percent of eluted faction corresponding at several boiling points and different samples.

Table 1 : weight percent of eluted fraction for feed and effluents obtained using extended SFC.

Boiling point (°C)	Feed A (vacuum residue) % w/w	Effluent HDM % w/w	Effluent HDM - HDS % w/w
500	0.58	0.57	4.98
600	28.3	39.72	11.07
700	63.66	70.54	51.39
750	74.39	78.89	78.53
800	81.91	84.52	88.5

As opposite to the GC simdis, SFC simdis extends the range of this application up to nC_{162}, providing better quantitation of conversion in heavy petroleum-fraction processing.

Conclusions

SFC is well adapted to the characterization of heavy hydrocarbons because of the solvating properties of supercritical fluids and could be applied in routine simulated distillation for extending the range of the technique. Besides, work is on progress to take benefit from detection facilities of SFC to perform specific Simdis curves.

References

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