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On-line introduction of high-pressure gas–liquid sample for capillary gas chromatographic analysis

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Abstract

An on-line sample introduction technique in capillary gas chromatograph (CGC) for the analysis of high-pressure gas–liquid mixtures has been designed and evaluated. A sample loop of 0.05 μL and a washing solvent loop of 0.5 μL are mounted on a 10-port switching valve, which serves as the injection valve. A capillary resistor was connected to the vent of sample loop in order to maintain the pressure of the sample. Both the sample and the washing solvent are transferred into the split-injection port through a narrow bore fused silica capillary inserted into the injection liner through a septum. The volume of the liner is used both as the pressure-release damper and evaporation chamber of the sample. On-line analysis of both reactants and resultants in ethylene olimer reaction mixture at 5 MPa was carried out, which demonstrated the applicability of the technique.

Keywords: Injection methods; Ethylene oligomerization; Sample preparation; Alkenes

1. Introduction

Determination of phase composition of both reactants and resultants at real reaction conditions involves sampling-analyzing process. The accuracy of the analysis is very important for quality control in chemical plants and synthetic industries. However, high-pressure gas–liquid mixtures from chemical reactors are difficult to analyze quantitatively owing to the sampling error and injection discrimination. Traditional methods [1–3] involve cool down the sample and release the pressure of it, which is further degassed and the gas and liquid fractions are analyzed separately. The data of the two fractions are later recombined to determine the total composition. The problems of the procedure are the absorption of heavy components on the wall of the transport pipelines or sampling tank [4], the escape of dissolved gases or light components in the liquid phase during sampling, and the mass discrimination at the GC injector when the boiling point range of the sample is wide, resulting in large errors on quantitation. The discrimination between heavier and light components in quantitation is not uncommon for samples having wide range of boiling point such as crude oils and in oligomerization reaction. Another problem is the transportation of expanded samples for GC analysis without loss of separation efficiency (due to large dead volume along the chromatographic circuit).

The analysis of high-pressure samples had been applied in studies of phase equilibrium [5–10]. Lockemann et al. [5–8] reported an on-line determination of equilibrium compositions with the help of special designed valves; Danesh and Todd [9] introduced a full stream sampling technique for compositional analysis of high-pressure fluids by using a solvent trapping technique and uniphase sampling to a gas chromatograph; Galicia-Luna et al. [10] used a compressed air-monitored sampler injector for extracting and injecting phase samples into the carrier gas circuit of a gas chromatograph.

An automatic on-line gas chromatographic method was used for monitoring the mixture of natural gas with liquefied petroleum gases under high pressure [11]. The compressed samples from gas and liquid phases were isolated into high-pressure sampling loops through a series of switch-

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ing valves before their expansion into variable-volumes syringes. The expanded samples were then analyzed by GC to give the distribution of hydrocarbon components in the respective phases. A high-pressure microcatalytic pulse reaction system equipped with a high-pressure gas chromatograph was presented [12]. Dahl et al. [13] reported an injection method for the compositional analysis of oil sample at high pressure. In their setup, transfer lines were pressurized with N_2 to achieve the original sampling pressure, and a mini-pump pushed a floating piston of the oil sampler to introduce the sample into the loop of the liquid valve. The oil sample was depressurized after injection. Both the sample loop and the transfer line must be heated to vaporize the residue of samples as completely as possible after injection.

α-Alkenes are widely used in resin copolymers, plasticizers and many fine chemical products [14]. It is important to measure the distribution of α-alkenes in situ during the process of α-alkene production. Off-line sampling and phase separation followed by capillary GC (CGC) analysis [15–17] had been adopted, which gave raise to problems mentioned above.

The present work is aimed at on-line analysis of the composition of high-pressure reactants and resultants in one operation. Non-depressurization sampling and valve injection-liner chamber expansion technique were utilized. Comparative study was carried out by using this technique and syringe on the analysis of synthesized α-alkenes from a reactor.

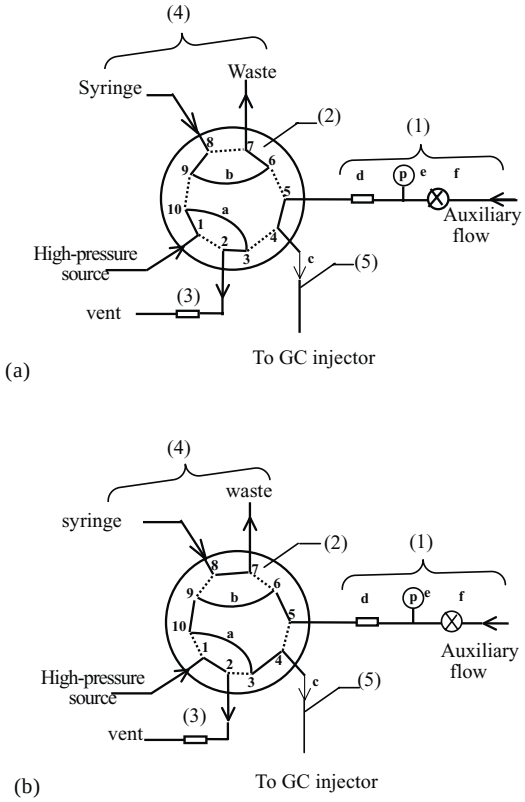

Fig. 1. Schematic diagram of the device for on-line injection of high-pressure sample: (a) sampling position; (b) injection position; (1) auxiliary flow; (2) 10-port valve; (3) resistor; (4) washing solvent; (5) transfer capillary.

2. Experimental

2.1. Apparatus

The direct injection device (DID), as shown in Fig. 1, consists of a Valco 10-port 2-position valve used for HPLC; a sample loop made of a 25 μm i.d. capillary tubing, a solvent loop, a capillary resistor connected with one vent of the valve in order to maintain the pressure of the sample; a constant flow controller for auxiliary carrier gas; and a transfer capillary introducing the sample and the solvent directly into the GC injector. A Perkin-Elmer Autosystem XL gas chromatograph (Norwalk, CT, USA) equipped with a flame ionization detection (FID) system and a split/splitless injector was used in this study. A quartz liner with an internal volume of 1.25 mL was used in the injector. A Shimadzu GC-17A system (Shimadzu, Kyoto, Japan) equipped with a FID system and a split/splitless injector was used for on-line determination of the high-pressure samples on site. A quartz liner with an internal volume of 0.85 mL was used in the injector. The split ratio was 20:1. Carrier gas was nitrogen at constant flow rate of 4 mL/min. The conditions for all GC analyses were as follow: initial column temperature 35 °C and hold for 6 min, then programmed at 15 °C/min to 250 °C and hold; injector temperature 250 °C; detector temperature 280 °C. A 30 m × 0.53 mm i.d., 0.6 μm OV-1 (Dalian Sci-Tech Instruments, China) and a 30 m × 0.53 mm i.d., 0.6 μm HP-1 capillary column (Agilent, USA) were used for the Perkin-Elmer Autosystem XL gas chromatograph and the Shimadzu GC-17A gas chromatograph, respectively.

A 1 μL liquid syringe (Shanghai Medical Laser Instruments) was used for comparative study.

2.2. Reagents

n-Pentane (>99.5%) was obtained from Shenyang Lianbang Solvent Factory. The sample of synthesized α-alkenes (1 atm, room temperature; 1 atm = 101,325 Pa), was used as the test sample for comparison of the precision between the above-mentioned method and the syringe injection. The high-pressure sample of synthesized α-olefin hydrocarbons (50 atm, 100 °C) was the real sample from a reactor on-line. All the samples were from the Institute of Daqing Petrochemical Co. (Daqing, China).

2.3. Operation procedure

Fig. 1a shows the loading position of the valve. A high-pressure sample is flowing through the sample-loop

(a) of the valve from a reactor and vent through a capillary resistor (3), which maintains the pressure of the sample in the sample-loop as that of the reactor. The sample in the transfer line between the reactor and the valve is in liquid state, preventing any deposition of heavy compounds on the wall. A washing solvent is injected into the solvent loop (b) by a syringe. Fig. 1b shows the injection position of the valve. The auxiliary carrier gas (1) drives the solvent (b) and the sample (a) directly into the GC injector liner through the transfer capillary (5). The pressure of the sample is released in the chamber of the liner. Both the sample and the washing solvent are evaporated in the liner without loss of any compounds.

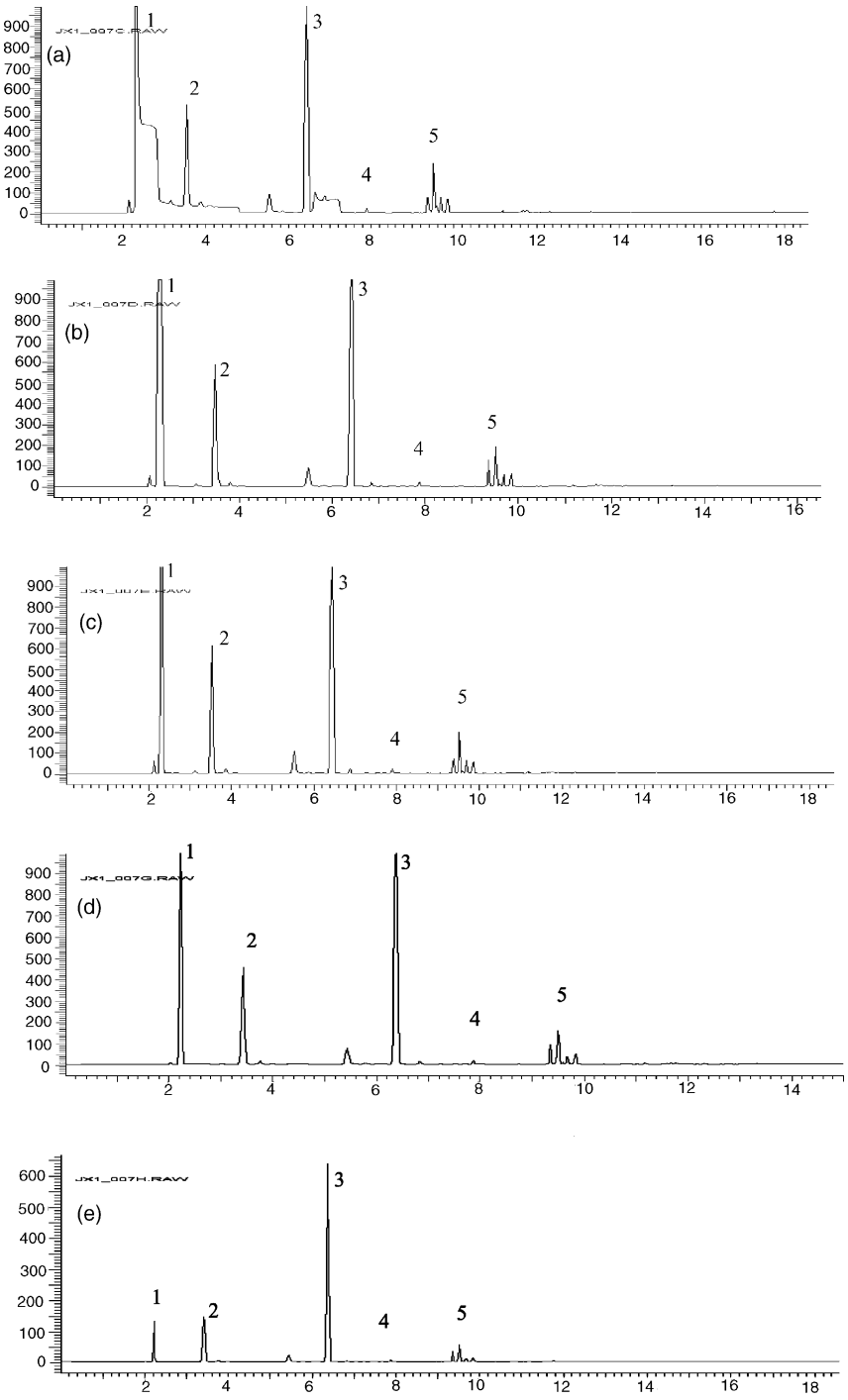

Fig. 2. Chromatograms of different injection time: (a) 2.5 min; (b) 10 s; (c) 5 s; (d) 2 s; (e) 1 s. Peak identities: (1) solvent; (2) C_6^{2-}; (3) C_7^{0}; (4) C_8^{2-}; (5) C_{10}^{2-}. Time scale in minutes.

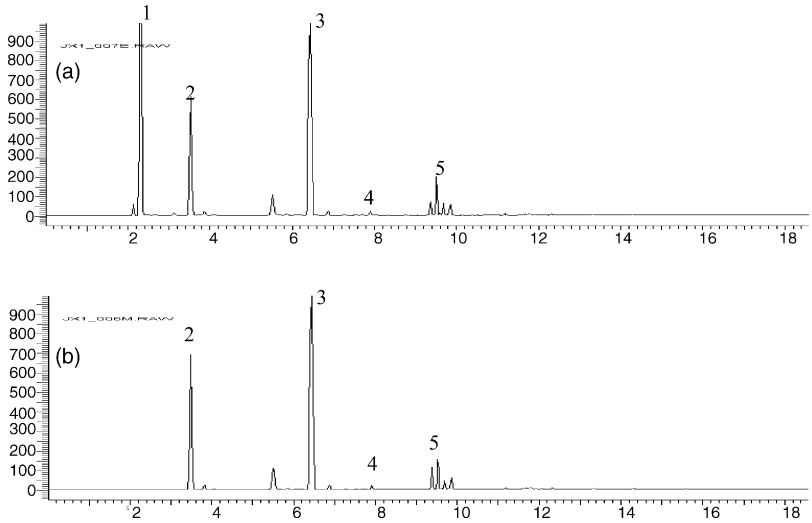

Fig. 3. Comparison of chromatograms with different injection mode under ambient pressure: (a) on-line valve-injection; (b) syringe-injection. Sample volume: 0.05 μL. Peak identities: (1) solvent; (2) C_6^{2-}; (3) C_7^0; (4) C_8^{2-}; (5) C_{10}^{2-}. Time scale in minutes.

3. Results and discussion

3.1. The washing solvent

The use of the washing solvent is to remove any remaining sample left in the sample-loop and transfer it with the sample into the GC port. The solvent should have good solubility to sample and should not interfere with the components of sample and the peaks in chromatogram. *n*-Pentane was chosen in this work, since it was fulfill the requirements mentioned above for sample we analyzed.

3.2. The volumes of the loops and injection time

Because of the very limited sample capacity of the capillary column and the concentrated sample from a reactor, the injection volume of a sample should be less than 0.2 μL. Sample volumes of 0.2, 0.1 and 0.05 μL were tested, and the smallest one was chosen. A 12 cm × 25 μm i.d. fused silica capillary tubing with internal volume of 0.05 μL was used as the sample-loop. The volume of washing solvent is determined by two factors. First, it shall be large enough to wash the sample-loop to eliminate any carryover of samples; second, it shall not exceed the limit of the expansion volume of the liner when it is evaporated. Solvent volumes of 0.2, 0.5 and 1 μL of *n*-pentane were tested, and 0.5 μL was chosen since excessive solvent resulted in too large solvent peak and may overlap with the sample peaks. A 13 cm × 75 μm i.d. fused silica capillary tubing with inner volume of about 0.5 μL was used as the solvent-loop. The inertness and smoothness of the inner wall surface of the capillary tubing prove to be adequate as both sample and solvent loops. We also studied the injection time and peak broadening effects. Fig. 2 shows the chromatograms of different injection time. The chromatograms indicated that if injection time is too long, say 2.5 min, a large tailing solvent peak was found (ref. Fig. 2a). In contrast, when the injection time is too short, say 1 s, a loss of sample is observed.

3.3. The resistor

It is very important to keep the pressure in the sample transfer line and the sample loop as that of the high-pressure source in order to keep the composition of sample in the loop the same as that of the source. A 30 cm × 50 μm i.d. fused silica capillary was used as the resistor, which provides adequate resistance to pressure of 50 atm.

3.4. The flow rate of auxiliary gas

The auxiliary gas (1) forces the washing solvent and the samples into the GC injector and acts as an auxiliary carrier gas afterwards. It is operated at constant flow condition. The expansion volume of the sample during the transfer from the sample loop to the injector is only a few microliters, causing minor influence on the injection process. We studied the flow rate of the auxiliary gas, the solvent peak shape and the separation efficiency of the system, and found that the optimal flow rate of auxiliary gas was 2 mL/min. Higher than 4 mL/min would exceeds the optimal flow rate of the

Table 1
Normalization results (%, w/w) using (A) syringe-sampling and (B) valve-sampling

Compound	Method A (%, w/w)	Method B (%, w/w)	R.S.D. (%)[a]
C_6^{2-}	22.92	22.46	1.6
C_7^0	68.28	67.85	0.3
C_8^{2-}	0.36	0.45	3.7
C_{10}^{2-}	7.42	7.95	2.6

[a] Seven replicates of on-line valve-injection.

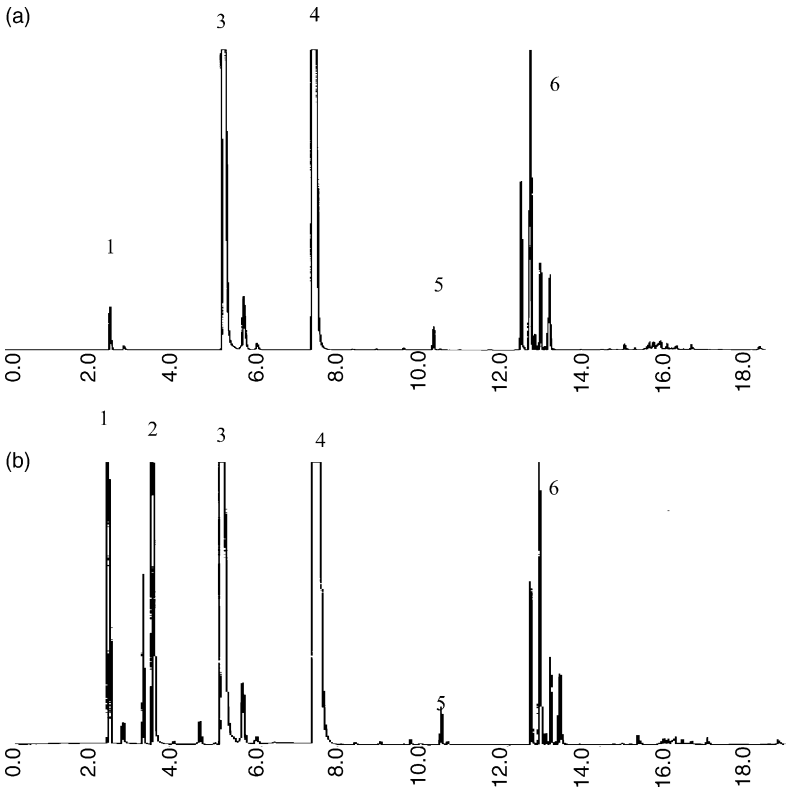

Fig. 4. Comparison of chromatograms of reactants on different system: (a) off-line syringe sampling under ambient pressure; (b) on-line valve sampling at pressure of 5 MPa. Peak identification: (1) C_2^{2-}; (2) solvent; (3) C_6^{2-}; (4) C_7^{0}; (5) C_8^{2-}; (6) C_{10}^{2-}.

separation column, and lower than 1 mL/min would increase the injection band width.

3.5. Comparison between two injection methods

At optimal system conditions, the sample of synthesized α-alkenes (1 atm, room temperature) containing C_6^{2-}, C_8^{2-} and C_{10}^{2-} were analyzed by both the on-line method and traditional syringe injection. Chromatograms are shown in Fig. 3, and the quantitative results and precision are shown in Table 1. The data in Table 1 proved that comparable results are obtained by both methods for liquid sample. The data in Table 1 shows satisfactory results for quantitation.

3.6. Application of on-line analysis of high-pressure samples

In the Kiggla-Natta reaction, ethylene was used as the unique reactant, which is polymerized to α-hexene and other by-product with proper catalyst dissolved in the solvent of *n*-heptane. The system is isolated from water and oxygen, and is kept at 5 MPa during the reaction. The concentration of ethylene dissolved in the liquid phase during the reaction is a very important parameter for process control. However, it is impossible to analyze the real concentration of reactants and resultants by off-line sampling method. Fig. 4a shows the resulting chromatogram by off-line sampling and syringe injection. For on-line monitoring, a probe is placed into the liquid phase inside the high-pressure reactor vessel, and is connected directly with the on-line sampling device through a 1/16 in. stainless-steel tube (1 in. = 2.54 cm). The chromatograms obtained from the on-line sampling is shown in Fig. 4b. The difference of Fig. 4a and b is remarkable, especially for volatile compounds. The content (%, w/w) of ethylene was only 0.18% by off-line syringe injection method, and was 9.22% by on-line valve direct-injection method (Table 2).

Table 2
Comparison between (A) off-line syringe sampling at ambient pressure and (B) on-line valve sampling at 5 MPa

Method	Components and normalization results (%, w/w)				
	C_2^{2-}	C_6^{2-}	C_7^{0}	C_8^{2-}	C_{10}^{2-}
A	0.18	30.54	65.70	0.10	2.82
B	9.22	27.58	60.56	0.08	1.89

4. Conclusion

The method described allows rapid on-line determination of high-pressure samples by capillary gas chromatography. It completes the sampling and sample injection in one operation and provides reliable quantitative results simply by

normalization (%, w/w) method; it avoids mass discrimination between volatile and semi-volatile components in a high-pressure two-phase system during sampling. The device is very simple but reliable, and can be used for on-line analysis of high-pressure samples from reactors or pipelines.

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