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Automatic on-line gas chromatographic monitoring of mixing of natural gas with liquefied petroleum gases under high pressure

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ABSTRACT

An automated system was constructed for the on-line monitoring of the mixing of natural gas with liquefied petroleum gases under different temperature (10–45°C) and pressure (5–20 MPa) regimes. After the system was equilibrated, compressed samples from gas and liquid phases were isolated into high-pressure sampling loops through a series of switching valves before their expansion into variable-volumes syringes. The expanded samples were then analysed by a rapid-scanning, dual-channel gas chromatograph to give the distribution of hydrocarbon components in the respective phases.

The system was devised to overcome the problems associated with on-line sampling and GC monitoring of mixtures from reactions of low-molecular-mass hydrocarbons under high pressure where phase changes can occur. This system features rapid sampling under pressure from the phases; accurate sampling of small volumes (50–500 μl) from these phases without disturbing the reaction equilibrium; volume expansion of the compressed samples (maximum pressure at 20 MPa) so they are amendable to GC analysis; transport of the expanded gases to GC with minimum peak broadening; and finally, very rapid GC analysis (<1 min).

The system is computer-controlled to enable fully automatic operation. Data points from the respective phases of a mixture under a temperature and pressure regime can be obtained in a fraction of time required with conventional procedures.

INTRODUCTION

The phase behaviour of a hydrocarbon mixture depends on the temperature and/or pressure of the system. The mixture can exist in a single phase as a liquid or a gas, or a gas–liquid binary phase, or even a single supercritical fluid phase when the operating temperature and pressure is greater than the critical point of the mixture [1]. Therefore in examining a mixture of hydrocarbons under different temperature–pressure regimes it is important to know how many phases are present and the distribution of the components in these phases.

The automation of on-line GC monitoring of reaction of hydrocarbons under high pressure has always been a difficult area in that a number of obstacles have to be overcome: rapid and accurate sampling from different phases from the system under pressure; *in situ* volume expansion of the compressed samples without selectively precipitating the heavier components from the mixture in a phase (caused by the Joule–Thomson effect [2]); transport of expanded gases for GC analysis without loss of separation efficiency (due to large dead volume along the chromatographic circuit); and rapid GC analyses.

Previous studies [3,4] on gas mixtures under pressure usually involved separate manual operations of sampling, expansion and analysis. A preferred method was to trap the sample from a phase into a gas bag that resided inside a water-filled container [5]. The amount of sample taken was then estimated from the mass of the water

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displaced from the container after its expansion. The gas bag was then removed and an aliquot of the expanded gas was analysed by GC. This procedure, while it gave accurate results, was still cumbersome and time-consuming, sometimes requiring large volumes being sampled from the phases. The reaction equilibrium was often disturbed which prevented subsequent samples being taken from the same experiment. To obtain a complete reaction profile within a temperature–pressure range, it was necessary sometimes to run several parallel experiments that could be curtailed at different reaction intervals.

In the past, studies [6,7] on mixtures of hydrocarbons at different temperature and pressure regimes mostly have been confined to the phenomena of vapour–liquid equilibria. Recently, O'Brien *et al.* [8] have reported that the solubility of methane in low-molecular-mass hydrocarbons can be increased at moderately elevated pressure (<8 MPa). An implication to this finding is the possible enhancement of storage of natural gas (NG) in liquefied petroleum gases (LPG).

In Australia about 5% of vehicles are already fuelled by LPG comparing to the relatively fewer vehicles that are using NG (as compressed NG). The reasons for this are largely due to the low amounts of the fuel which can be carried onboard and the danger perceived by the public of carrying a highly pressurised gas in a vehicle. An increase in the usage of NG will only come when both the storage capacity and onboard transport safety can be improved. Australia has one of the largest reserves of NG in the world. An increase in its usage for transport purposes will not only reduce the expenditure for imported oils, but also will have positive impact to the environment since NG-powered vehicles emit lower hydrocarbons, carbon oxides, and smokes.

LPG is well-suited as a storage solvent for NG. It is abundant, being a cheap offcut in oil refining and also as an "impurity" from natural gas wells. Under moderate pressure and at normal temperature, LPG can be transported in a liquid form, and when released at atmospheric pressures at relatively low temperature it vaporises and can be handled as a gas. It is therefore far safer to store NG in LPG at relatively low pressure than the pressure required in compressed NG. Further, instead of using LPG only as a storage solvent, LPG–NG mixtures may be used as an alternative transport fuel. This would overcome the costly operation of having to separate the NG from the storage medium before its use. In using these mixtures it is envisaged that only minor modifications would be required to the existing technology for LPG and NG. As a combined fuel, LPG–NG mixtures would also have higher energy densities than NG or LPG alone [9].

This project at CSIRO is a study on the storage capacity of NG in LPG at different temperatures and pressures. The work will also examine whether LPG–NG mixtures can be used as vehicular fuels, in particular the phase and composition changes during the emptying of the storage tank. This is the first of a series of papers on the storage of NG in LPG. This paper concentrates on the construction of an automated system that can monitor the changes in distribution of hydrocarbons in the different phases of mixtures in a reaction vessel under varying temperature and pressure regimes. The work reports the obstacles involved in interfacing of a rapid-scan GC to a high-pressure gas mixing system. *In situ* GC is an integral part of the automated system.

EXPERIMENTAL

Materials

Propane (>99% purity) and a standard gas mixture consisting of carbon monoxide (4.5 mol%), carbon dioxide (8.99%), methane (28.28%), ethane (5.11%), propane (29.0%), propene (9.42%) and butane (14.7%) were obtained from Matheson (CA, USA). The NG was obtained from AGL Sydney (Sydney, Australia) and was compressed in the laboratory to 20 MPa. LPG was purchased from Elgas (Sydney, Australia).

Two other gas standards were used: an *n*-alkane mixture (C_1–C_6, 1 ppm (v/v) of each in helium), and a mixture containing carbon dioxide, carbon monoxide, oxygen and hydrogen. Both were purchased from Alltech (Sydney, Australia).

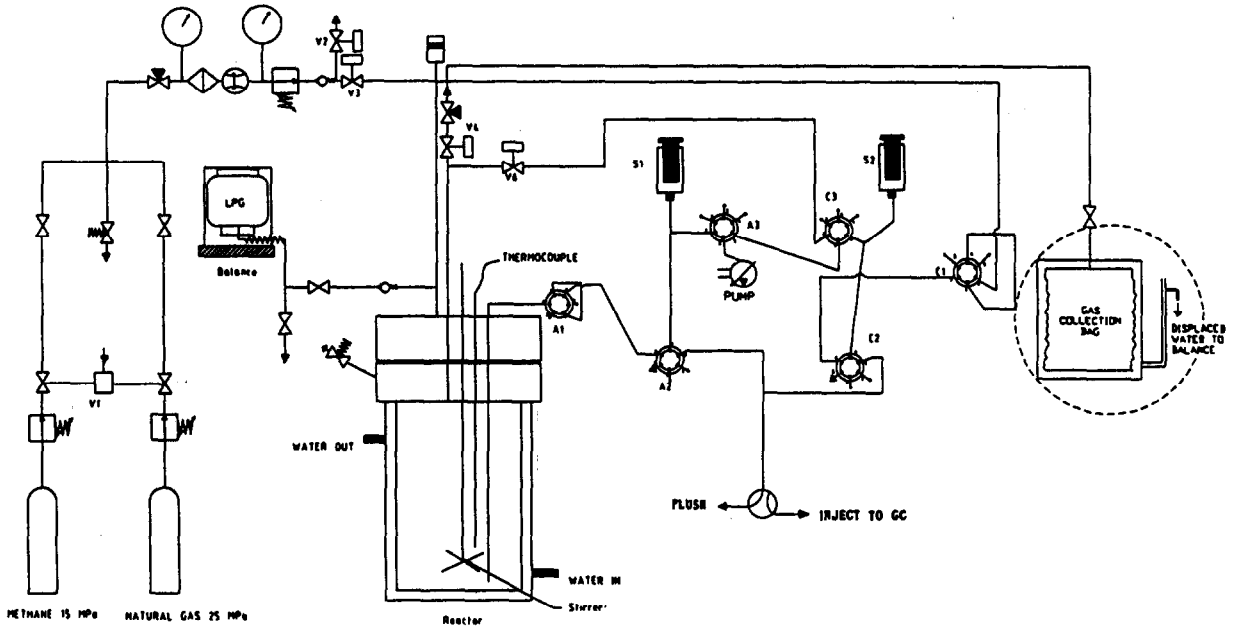

Fig. 1. The schematic of the GLS rig used for this work. Two sets of two way switching valves (A1/A2/A3 and C1/C2/C3) are used for manipulating samples from the liquid and gas phase of the mixture. S1 and S2 are variable-volume syringes. For gas discharge experiments the gas collection system is connected to V_4 as showed by the broken circle in the figure.

Equipment

The schematic of the apparatus constructed for this study is shown in Fig. 1. The storage solvent such as propane, butane or LPG was introduced first into the reaction vessel (316 stainless steel 300 ml packless autoclave from Autoclave Engineers, Erie, PA, USA). To ensure that only the liquid phase was used, the hydrocarbon was metered into the reaction chamber through a valve from an inverted cylinder sitting on a Mettler PM 34 Delta Range balance (Mettler Instrument Co., NJ, USA). NG or methane was then used to fill the reaction vessel to a preset pressure via a Brooks Mass Flow Meter (5850E 1-l CH_4/min, Brooks Instrumental Division, Hatfield, PA, USA). The exact mass ($M = ftd$) of the latter gas used was calculated from its flow rate at the set pressure (f), the duration of filling (t), and density (d). The temperature of the autoclave was maintained at a constant temperature by recirculating water from a Model SPE. TBC Thermoline waterbath (Thermoline Scientifics Equipments, Sydney, Australia) through a water jacket surrounding the autoclave. A 1.5-mm diameter type "T" thermocouple was used to monitor the temperature.

The mixture in the reaction vessel was stirred to equilibrate the reaction. The stirrer in the autoclave was driven by a 1/2 Hp DC shunt motor (Aust. Balder, Sydney, Australia) with a Multi-Driver speed controller (K. B. Electronics, NY, USA). Changes in pressure were monitored during stirring and the reaction is equilibrated when there is no further change in pressure. Fig. 2 shows a typical pressure–time profile. Although the reaction was equilibrated in few minutes, stirring was maintained throughout the duration of the experiment to ensure that there was no phase change.

Samples from the phases were trapped separately into fixed-volume loops (250 and 500 μl) of switching valves (Rheodyne 7000ARV with actuator, Rheodyne, Cotati, CA, USA). The sampling lines and loops were flushed twice before actual sampling. The samples in the loops then were expanded into previously evacuated variable-volume syringes (VVSs) after equilibration. Aliquot of the expanded phases was then inject-

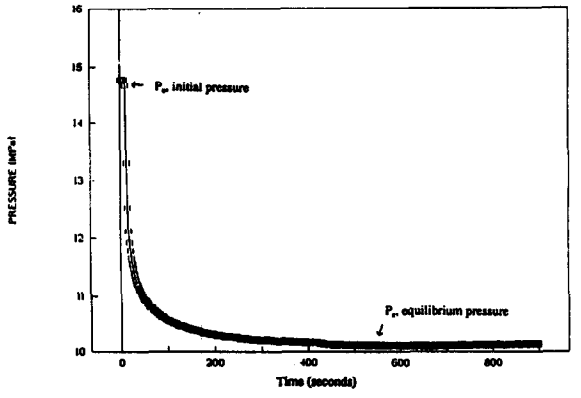

Fig. 2. Pressure–time profile of LPG–NG mixture during stirring (473 rpm) at 15 MPa and 20°C. The masses of LPG and NG are 40.2 and 34.54 g, respectively.

ed into the rapid-scan M200-D gas chromatograph (MTI, Fremont, CA, USA). Separate transfer lines and expansion syringes were used for the two phases to avoid cross contamination.

The VVSs were laboratory-made for expanding compressed samples from the two phases. Glass airtight syringes (SGE, Australia) of 50 and 100 ml were used respectively for expanding samples from the gas and liquid phase. The movement of the syringes was controlled by stepmotor drivers (200 steps/revolution) via lead screws. A set of two "safety" microswitches were positioned at the upper and lower expansion limits of the syringe. The first limit was the software control of syringe movement and the second was connected to the interlock of the motor that cuts off the motor once the microswitch has been activated. This double safety feature was necessary to ensure that the plunger of either syringe does not travel beyond the extreme limits.

Venting experiment

For the gas discharge experiment the gas collection system (showed by the broken circle in Fig. 1) was connected to valve V4 of the rig (hence referred as the gas–liquid solubility rig (GLS) in Figure 1). As the gas was discharged from the reaction chamber into the gas bag an equal volume of waster was displaced from the Perspex box.

Operation of the switching valves

Venting/flushing of the transfer lines and sample loops, evacuation, filling and emptying of syringes, and transport of expanded samples for GC analyses were controlled by two separate sets of serially linked 2-way switching valves. Each set of three valves controlled all the operations on a phase. Table I gives an example of

TABLE I

COMBINED VALVE CONFIGURATIONS FOR SAMPLING FROM THE LIQUID PHASE OF THE GAS–LIQUID SOLUBILITY RIG AND INJECTION OF ALIQUOT ONTO THE GC SYSTEM

Operation sequence	Switching valve configuration						Syringe movement	GC inlet valve	Function
	A1	A2	A3	C1	C2	C3			
1[a]	1	0	0	0	0	1	None	Flush	Fill sampling loop
2[a]	0	0	0	0	0	1	None	Flush	Expel sampling loop
3	1	1	1	0	0	1	Up	Flush	Fill loop and devacuate syringe and sampling line
4	1	1	0	0	0	1	None	Flush	Isolate syringe from pump
5	0	1	0	0	0	1	None	Flush	Expand liquid from loop to syringe
6	0	0	0	0	0	1	Down	Inject[b]	Inject expanded gas to GC system
7	0	0	0	0	0	0	None	Flush	Reset valve configuration and flush GC system
8	0	0	0	0	0	0	Up	Flush	Reset syringe to maximum volume

[a] The combined operation of sequences 1 and 2 is used for flushing the sampling loop.
[b] The GC inlet is switched to "Inject" after the sampling lines have been flushed with expanded gas.

the configurations of a set of valves for manipulating a liquid phase from the reaction chamber of the GLS rig. The movement of a valve is given as either "0" or "1" in the table, representing the valve configurations shown in Fig. 3. A similar sequence of operations was required for manipulation of samples from the gas phase. As indicated in Fig. 1, valves A_1, A_2, and A_3 control all the operations on the liquid phase and C_1, C_2, and C_3, on the gas phase.

The movements of the valves were computer-synchronized. Fig. 4 shows the combined movements of the valves during the filling of the sampling loop from the liquid phase (top) and the simultaneous evacuation of the transfer lines and the VVS just before the expansion of the compressed sample (bottom). One or more valves can be switched during an operation.

Evacuation of the syringes and transfer lines was actuated by switching the appropriate valves in-line with the pump that was left on throughout the experiment.

Operating conditions for M200-D gas chromatograph

The M200-D GC system can be operated isothermally only and therefore required two separate columns for complete separation of all the hydrocarbon components in the LPG–NG mixtures. GC analysis under isothermal conditions gives a faster turnaround time than temperature programming since no column temperature re-equilibration is required. On entering the GC system, the sample is split for analysis on the two columns. Channel A of the M200-D has a 4-m MS-5 column which was operated at 100°C with column head pressure of 14.5 p.s.i. (1 p.s.i. = 6894.75 Pa), and channel B, an 8-m PoraPlot Q column operated at 135°C and a column head pressure of 27.5 p.s.i. The analysis times for channel A and B were 60 and 80 s, respectively, and the sampling time (equivalent to the amount injected to the microchamber) was 5 ms.

A 2-μl A315 precolumn filter (Upchurch Scientific, Oak Harbor, WA, USA) was placed between the GC inlet switching valve and the

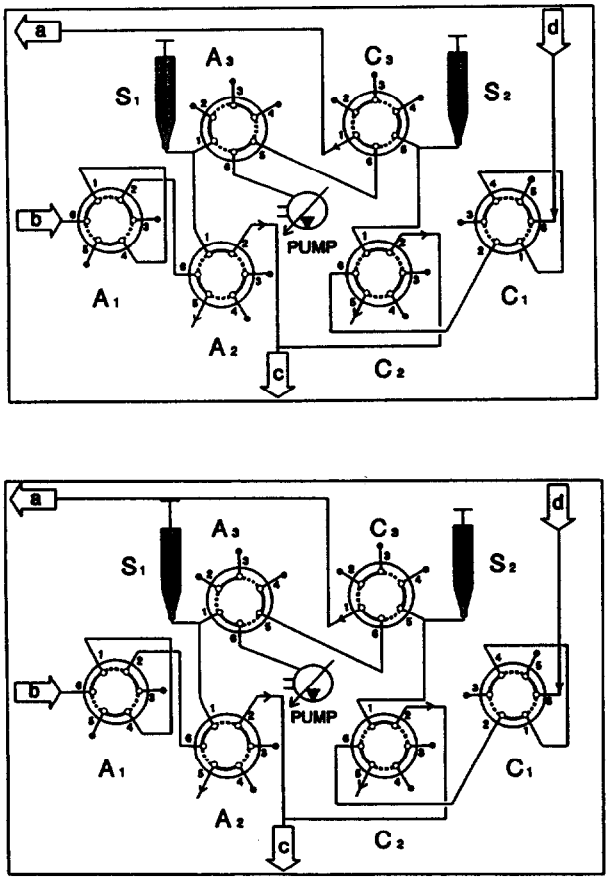

Fig. 4. Combined movements (top) of valves for filling of sampling loop (connecting ports 1 and 4 of A_1) from the liquid phase and (bottom) evacuation of transfer lines and syringe before the expansion of the trapped sample in the loop. Line connectors in the figure, "b" and "d", are connections from liquid and gas phases. Connector "c" comes from the GC system and "a" from the transfer line joining V_6.

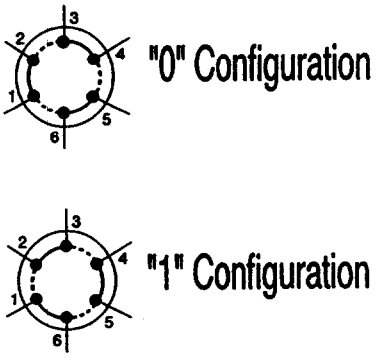

Fig. 3. "0" and "1" configurations representing position of switching valves are referred in Table I.

inlet of the M200-D GC system. This is important in preventing the blockage of the fine orifice of the columns by particulate matter.

No special setting of the detector condition was needed for the M200-D; the only requirement was the switching on of the detector with the sensitivity set on low, medium, or high level. These functions are controlled through the EZ-Chrom software.

Sampling of expanded gases from VVSs to the M200-D GC system

The M200-D GC system has a built-in 8-μl microchamber which is filled by drawing sample from the flowing stream by the built-in micro vacuum pump only when the GC is activated. In the GLS rig, the expanded gas from either of the two VVSs was expelled to waste through an adjustable needle valve via a 2-way switching valve (Fig. 5). In the "inject" mode (top) the GC inlet was positioned in-line with the flowing stream of the expelling gas and an aliquot was then extracted into the GC system for analysis. Otherwise, the GC inlet valve was left in the "flush" mode where the expanded gas was vented to waste continuously out the needle valve (bottom). The switching of the GC inlet valve to the GC system was computer synchronised with

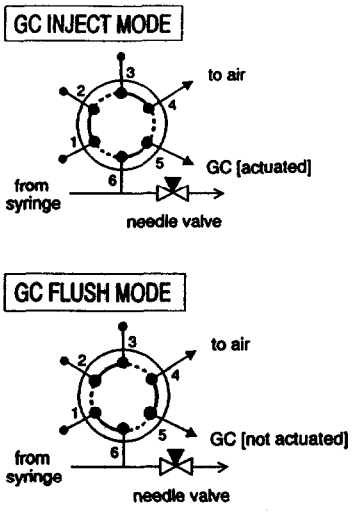

Fig. 5. The configuration of the GC inlet valve can be either in "inject" or "flush" mode. In the "inject" mode, the GC was connected directly to the flowing stream whereas in the "flush" mode it was diverted away.

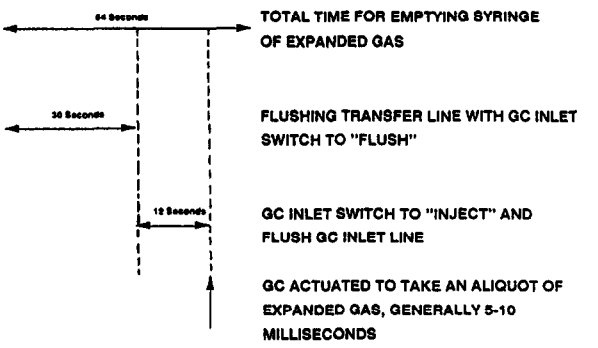

Fig. 6. Segmentation of events during the emptying of the expanded gas from the syringe.

the opening/closing of the microchamber of the M200-D. As shown in Fig. 6 the switching of the GC inlet valve to the "inject" mode occurs only after both the transfer line to the GC system and the GC inlet valve have been flushed with the incoming gas. The volume of expanded gas injected onto the GC columns depends on sampling time into the sample chamber of the M200-D and this is usually 5–10 ms.

Sampling from the expelling stream of the expanded gas at the immediate entrance of the GC system minimises peak broadening arisen from extra column effects.

Computer control

A software package (referred here as GLS software) was developed to synchronise switching of valves and for controlling various functions of the phases on the GLS rig. Fig. 7 summarizes the functions of the software. Manu-

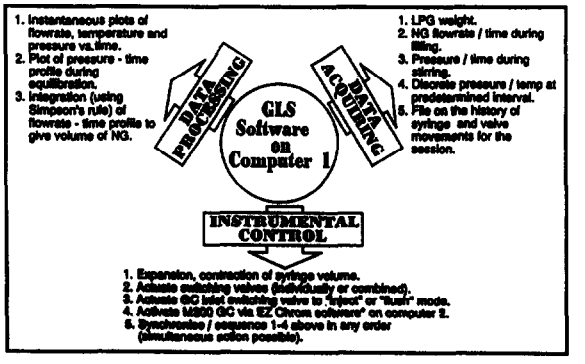

Fig. 7. GLS software used for controlling various functions on the GLS rig. *Commerical software from MTI, Freemont, CA, USA.

al operation of the system was automated through the instrument control section of the GLS software. In-build macros in the software allow considerable flexibility (point 5 under Instrumental Control in Fig. 7) in manipulating the action sequences during an automated run. Each macro is equivalent to a unique action and entails a line of valve operations such as that showed in Table I. These operations are carried out simultaneously. Macros can be sequenced in any order in a block to allow different combinations of actions in an automated run. For example, a sequence of eight actions listed in Table I can be programmed in macros and placed into a single block which then can be actuated by a single keystroke in the GLS software. Typically, for an automated run the program can be structured similarly to the flowchart given in Fig. 8.

Under the automatic mode the progress of a run can be viewed from a single screen. The experiment can be paused, stopped or even skipped to other sections of the program.

The GLS software provides an additional facility for low level testing of the interface boards. It was rarely used and employed mainly for fault finding and correction. The GLS software also provides a manual "screen" which shows the status of various parts of the GLS rig and allows the operator to interrupt the operation of the rig by pressing keystrokes on the computer.

A 640K XT computer (HYPEC, Sydney, Australia) was used to run the GLS software with special commercially available boards (I/O and ACD cards) for the controlling of the valves, stepping motors, and for data gathering. A separate computer (HPEC 386) was used for the gathering and analysis of GC data. The EZ-CHROM 200 version 3.1 (MTI) software was used for processing the GC data.

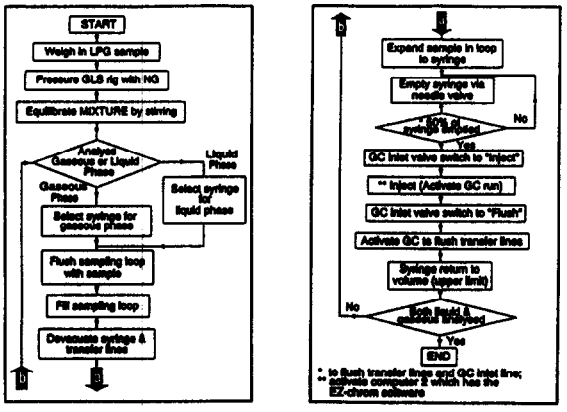

Fig. 8. The flowchart for the GLS software.

GC for analysing gas samples manually trapped in gas bags

A stand-alone GC system (Shimadzu 9C-9A) was used for analysing samples of gas mixtures which were trapped manually from the vapour and liquid phases. The GC system is a dual-injection system with both thermal conductivity and flame ionization detectors. For hydrocarbons, a 3-m alumina column (Alumina F-1, 80–100 mesh) was used with following GC conditions: helium carrier gas flow-rate at 25 ml/min, oven temperature 85°C and flame ionization detector at 280°C. For carbon dioxide, a 3-m Carbosphere (80–100 mesh) was used with the thermal conductivity detector with the following GC conditions: helium carrier gas flow-rate at 40 ml/min, oven temperature at 80°C and detector temperature 150°C (bridge current 150 mA).

RESULTS AND DISCUSSION

System automation

A number of obstacles have to be overcome to automate the system. Sampling from phases under pressure was carried out using fixed volume loops on high-pressure switching valves that have been used for HPLC. Since only a relatively small amount of sample was taken, there was no perceptible change of pressure in the reaction chamber during sampling and therefore there was a minimal disturbance of reaction equilibrium. Samples from phases were taken from different points in the reaction chamber, with the liquid phase drawn from the bottom and the gas phase from the top of the chamber. Separate sampling loops and switching valves were used for the two phases to minimise possible cross contamination. There was a notable drop of temperature of 4–6°C during the flushing of the sampling loops. An elapsing time of 3 min therefore was included in the automated cycle

for reestablishing the loop temperature before the actual sampling from the phases.

The compressed samples in the sampling loops were expanded in separate VVSs. The volumes of those syringes were fixed with respect to the sizes of the loops used. There was no notable change of temperature in the VVS during expansion, but a waiting period was included in the automated cycle to allow temperature equilibration.

Samples for GC were taken during the expelling mode of the VVSs. The actual sampling occurred immediately at the inlet orifice of the M200-D GC system after it had been switched in-line with the outgoing stream of the expanded gas from either of the VVSs. Sampling at this point minimised peak broadening since there was little or no dead volume along the chromatographic circuit.

Fig. 6 shows the actual sampling of the GC system from the expelling stream occurred during the emptying of the last 20% of the expanded gas from the syringe. The early portion of the expanded gas in the syringe was mainly to flush the GC inlet valve and transfer lines to the GC system. To gauge how representative was the sample taken from this segment of the syringe, samples were taken at the beginning, the middle, and near the end portion of the syringe during emptying. The peak area of these samples were compared and a maximum deviation of 2% was found. There was no evidence for the selective precipitation of the heavier components from the hydrocarbon mixtures. However, sampling from the early portion of the syringe did indicate that cross contamination occasionally occurred, especially when concentrations were varied widely between successive samples. Flushing was required to avoid this. Fig. 9 clearly illustrates the decrease of ghost peaks in the chromatograms after the system has been repeatedly flushed.

Finally, the M200-D rapid-scan GC system was used to provide rapid analysis. Samples from different phases of the reaction mixture in the GLS rig have to be analysed almost instantaneously once they have been sampled into the loops since prolonged waiting could cause phase separation [3]. Using two columns under isothermal condition, the M200-D GC system can analyse a mixture typically containing N_2, O_2,

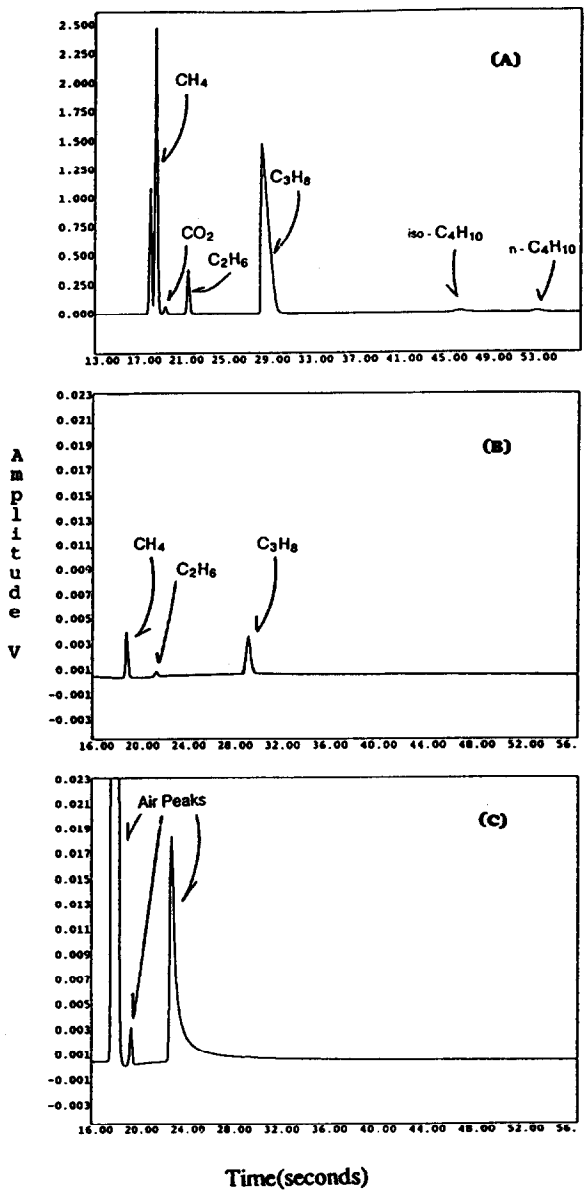

Fig. 9. Chromatograms illustrate the contamination problem: (A) is an injection of sample from the liquid phase of the reaction mixture; (B) shows ghost peaks from previous injection; and (C) after flushing the GC system with air.

CO, CO_2, CH_4, C_2H_6, C_3H_6, C_3H_8, n-C_4H_{10} and iso-C_4H_{10} in less than 80 s. This compares with a 50–60-min cycle time (reconditioning time for next run) required for the separation of the same gas mixture using conventional gas chromatographs. Fig. 10 shows a typical separation of a sample from the gas phase of the LPG–NG mixture. The column in channel A of the M200-

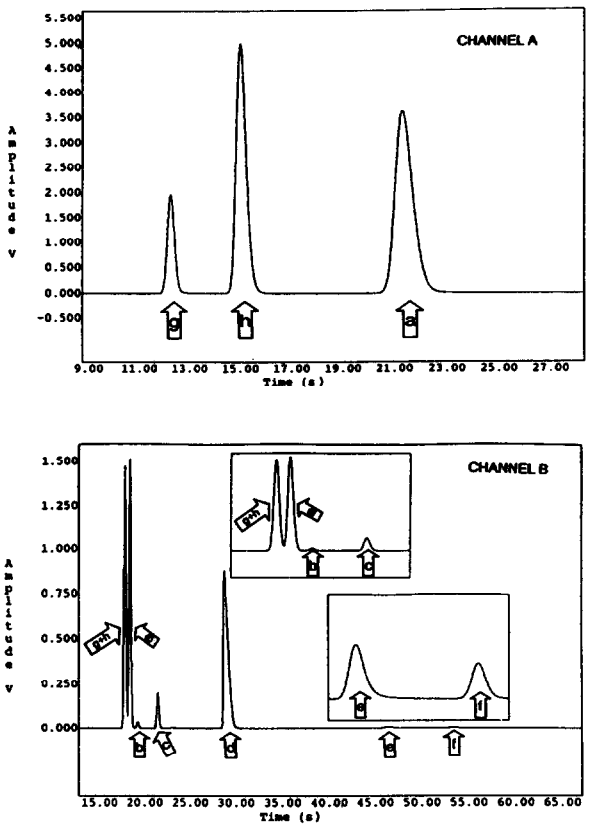

Fig. 10. Separation of sample from the gas phase of a LPG–NG mixture. The conditions of mixing was 12 MPa and 10°C using 59.9 g LPG and 22.21 g NG. a = Methane; b = carbon dioxide; c = ethane; d = propane; e = *n*-butane; f = isobutane; g = oxygen; h = nitrogen. The insets to the bottom figure show disproportionally small peaks that can be adequately handled by the EZ-CHROM software.

D was used for mainly detecting N_2, O_2 and CO. The CO peak, if present in the mixture, eluted immediately after the methane peak in channel A, and propene before propane in channel B. The EZ-CHROM software used with the M200-D gave a good dynamic range that allowed the detection of peaks of vastly different concentrations. This again is well illustrated in Fig. 10 where the concentration of *n*-butane and isobutane is approximately 100 times less than propane.

Automated cycle for determination of phase compositions

After mixing, samples from the respective phases of the reaction chamber were analysed. An automated cycle was then set up entailing the following actions: flushing of the sample loops and transfer lines; sampling from the phases; fixing the volumes of the VVSs; evacuation of the syringes; expansion of the samples in the loops into the VVSs; flushing of the GC inlet lines; transporting samples for GC analysis; and resetting of the switching valves and VVSs for the next run. Successive runs of a standard hydrocarbon mixture gave a maximum deviation of 3% for the smallest peak in the mixture.

Each cycle consisted of the actual GC analyses of the samples from the two phases plus flushing of the GC system after each analysis. For flushing, a sample of air was run through the system. Fig. 11 shows four sets of chromatograms resulted from each automated cycle. The complete cycle takes only 14 min.

The components of gases in the final mixture (using both phases) were mass balanced against those in the initial mixtures before mixing. Typically, in mixing NG with LPG at 10 MPa and 20°C, mass balances >99% was found for methane and propane, and >95% for ethane, *n*-butane and isobutane, and carbon dioxide. The good mass balances obtained here were mainly due to the closed nature of the automated GLS system, where losses were minimised, and the precise manipulations of the samples during its operation.

Results from the automated setup were also compared with those obtained using the conventional procedure where the gases from the phases were trapped into gas bags and analysed by a stand-alone GC system. A maximum deviation of 2% was found for the major components (methane and propane) and 4% for minor components of the mixture.

NG solubility in LPG

The reaction chamber of the GLS rig was never filled completely with liquid phase. Most of the time two phases existed in the chamber, with a liquid at the bottom and a vapour phase that occupies the space above the liquid. When the chamber is vented, some vapour leaves the chamber and immediately a certain amount of the liquid is evaporated to replace the lost vapour. However, the mixture in the chamber can become a single gas phase by reducing the

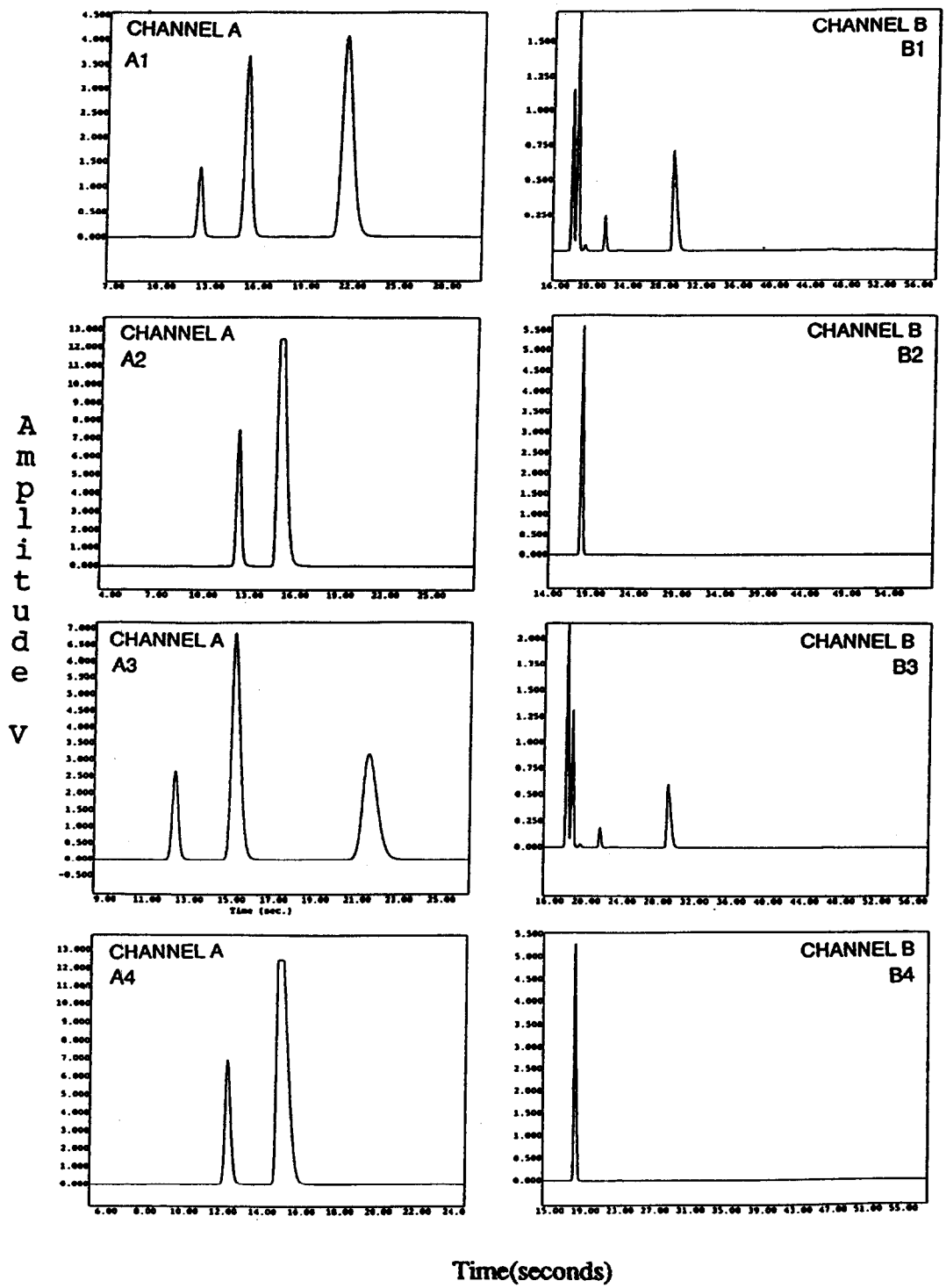

Fig. 11. Chromatograms from an automated cycle run: A1 and B1 are chromatograms of the liquid phase from channels A and B of the M200-D GC systems; A3 and B3 from the vapour phase; and A2, B2, A4 and B4 are chromatograms after the GC system has been flushed after each analysis.

pressure and/or increasing the temperature of the reaction chamber.

The dissolution of NG in LPG was calculated using the differential pressure profile of the stirring NG–LPG mixture similar to the one shown in Fig. 2. The formula used was:

$$n_g^i - n_g^f = \frac{(P_0 - P_s)(V_s^i)}{Z_0 R T_0} - \frac{(P_e - P_{sm})(V - V_s^f)}{Z_f R T_f}$$

where P_0 and P_e are pressures of reaction chamber before and after mixing; V is the volume of the vessel; V_s^i and V_s^f are volumes of liquid phase before and after mixing; P_s and P_{sm} are vapour pressure of the solvent before and after mixing; Z_0 and Z_f are compressibility factors before and after stirring; T_0 and T_f are temperature before and after stirring; n_g^i and n_g^f are the moles of the mixture in the gas phase before and after mixing; and R is the universal gas constant.

The above equation was further simplified to

$$C = \left[\frac{(M_r)_s}{W_s}\right]\left\{\left[\frac{W_g}{(M_r)_g}\right] - 273.15(P_e - P_{sm}) \times \left(\frac{V - \left(\frac{W_s}{d_f}\right)}{22.414 Z_f T_f}\right)\right\}$$

where $(M_r)_g$ and $(M_r)_s$ are the mean molecular masses of the gas and solvent mixtures; W_g and W_s are the masses of gas and solvent used initially; d_f is the density of the final solvent; and C is the dissolution concentration expressed in mol/mol.

The derivation of these formulae and a more detailed discussion on the solubility results will be the subject of a later publication. The second equation was used to calculate the solubility of NG in LPG with a given NG–LPG ratio (w/w) at a particular temperature and pressure. The saturated solubility was obtained by increasing the NG–LPG ratio until no more gas dissolved. Generally, the dissolution of NG at 20°C in LPG in a pressure range of 4 to 20 MPa increased the amount of gas stored. Enhancement factors were generally in the range of 1.4 to 1.65. That is, the amount of NG in a given volume could increase by half as much again when dissolved in a hydrocarbon solvent under the conditions specified. The increase in NG storage found here is less than that obtained when activated carbon was used as a storage medium [10]. An enhancement factor of 3 was obtained at 4 MPa using the best available activated carbon.

An example of solution of NG in LPG is demonstrated in Table II. At the equilibrium pressure of 3.31 MPa, the ratio of phase concentration of methane ($[CH_4]_{vap}/[CH_4]_{liq}$) was 2.43 but decreased to 1 at 11.49 MPa. While the ratio of phase concentration of propane ($[C_3H_8]_{vap}/[C_3H_8]_{liq}$) was 0.58 at the low pressure but increased to 1 at the higher pressure. Therefore, at pressure greater than 10.0 MPa the distribution of the components in both phases is the same. The finding here has important implication for how the stored mixture could be used. If the total mixture was to be used as a fuel then it would be preferable to mechanically maintain the system under high pressure (>10 MPa) so that the major components of the mixtures were evenly distributed in both liquid and gas phases. However, if the aim was to use the methane only and to cycle the hydrocarbon solvent as the storage medium then the operating pressure

TABLE II

DISTRIBUTION OF MAIN COMPONENTS IN RESPECTIVE PHASES OF MIXTURES AT DIFFERENT PRESSURE

Mixtures	Main components (in mol%)			
	CH_4	CO_2	$C_2H_6C_3H_8$	
NG (Initial)	90	1.6	8.2	0.2
LPG (Initial)	–	–	5.3	94
NG–LPG mixture at 3.31 MPa and 20°C				
Liquid phase	20.2	0.6	2.38	76.79
Vapour phase	49.1	1.2	2.4	47.31
NG–LPG mixture at 8.06 MPa and 20°C				
Liquid phase	47.78	1.16	4.45	46.62
Vapour phase	65.95	1.29	4.09	28.66
LPG–NG mixture at 11.49 MPa and 20°C				
Liquid phase	55.06	1.27	5.06	38.61
Vapour phase	56.78	1.34	5.37	36.38

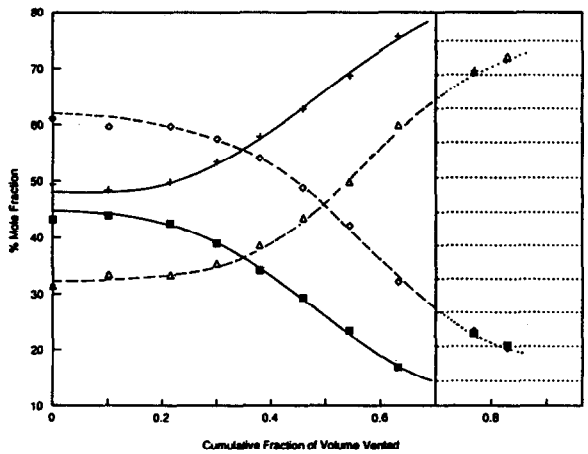

Fig. 12. Discharging profile of a NG–LPG mixture. The mixture was equilibrated at 8 MPa and 20°C using 60 g of LPG and 29 g of NG. The shaded area represents a change from a binary to single phase. ■ = CH_4(liq); + = C_3H_8(liq); ◇ = CH_4(vap); △ = C_3H_8(vap).

should be lower than the convergence pressure of the mixture.

Venting gas from the various two phase systems generally resulted in large variations in the vent gas molar composition until pressure fell to a point where a single gas phase existed. Fig. 12 shows a typical example. After gas was vented from the system there was a decrease of lighter hydrocarbon, CH_4, and an increase of the heavier gas, C_3H_8, in the remaining mixture. Both phases behaved similarly. A phase change occurred when 70% of the mixture had been vented and this is indicated in Fig. 12 by the abrupt coincidence of methane and propane concentrations for the two phases.

CONCLUSIONS

Studies on the dissolution of gases in hydrocarbon solvents must consider phase changes. Automation of *in situ* GC monitoring of the distribution of hydrocarbons in the different phases entailed the compressed samples from both phases to be in gaseous form at ambient temperature and pressure before they can be handled by GC. The use of rapid-scan GC and sampling at strategic locations in the system ensured rapid analysis with good sensitivity and minimum peak diffusion from reduced extra chromatographic effects. The automated system allowed the solubility of NG in LPG to be studied in one tenth of the time as that required with conventional procedures.

At equivalent temperature–pressure regimes the storage of NG was shown to be enhanced by more than 50% by dissolving it in LPG than when it was stored alone. However, NG was found to separate out the solvent during discharge when the system is continuously depressurised.

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REFERENCES

1 T. Ahmed, *Hydrocarbon Phase Behaviour*, Gulf Publ. Co., Houston, TX, 1989, Ch. 1.
2 R.A. Budenholzer, B.H. Sage and W.N. Lacey, *Ind. Eng. Chem.*, 31 (1939) 369–374.
3 C.J. Cowper and A.J. DeRose, *The Analysis of Gases by Chromatography (Pergamon Series in Analytical Chemistry*, Vol. 7), Pergamon Press, Oxford, 1983, Ch. 6.
4 K.J. Rygle, G.P. Feulmer and R.F. Scheideman, *J. Chromatogr. Sci.*, 22 (1984) 514–519.
5 G.C. Wall, *Proceedings of the 1st Australian Workshop on Oil Shale, Lucas Heights*, CSIRO Division of Energy Chemistry, Sydney, 1983, pp. 105–108.
6 S.K. Shibata and S.I. Sandler, *J. Chem. Eng. Data*, 34 (1989) 291–298.
7 C.-H. Kim, A.B. Clark, P. Vimalchand and M.D. Donohue, *J. Chem. Eng. Data*, 34 (1989) 391–395.
8 R.N. O'Brien, B. Turnham and S. Visaisouk, *Proceedings of the 1st International Conference and Exhibition on NGV —The New Direction in Transportation, Sydney, 1988*, pp. 1–9.
9 A. Melvin, *Natural Gas: Basic Science and Technology*, British Gas, Bristol, 1988, Ch. 6.
10 A. Chaffee and A. Pandolfo, *Extended Abstracts and Programme of International Carbon Conference, Paris, 1990*, pp. 246–247.