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Effects of Pressure in Coal Pyrolysis Observed by High Pressure TGA

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Abstract–High-pressure thermogravimetric analyzer was employed to investigate the effects of pressure on the thermal decomposition process, which is the very first step in most coal utilizing processes, and pyrolyzates from TGA were analyzed by on-line GC/MS. Results showed that pyrolysis of coal with steam under high-pressure conditions exhibited a slower reaction rate compared to the lower pressure conditions, and the effect is more evident at the high temperature region. Coal rank also exhibited a distinct effect on the pyrolysis rate such that a subbituminous coal showed a bigger effect by steam-addition and pressure than bituminous coals. Weathered coal sample illustrated a slower reaction rate compared to the unoxidized coal. In addition, the implication of pressure effects on pyrolysis has been described.

Key words: Pressure Effects, Coal, Pyrolysis, TGA, IGCC, PFBC

INTRODUCTION

Except conditions of extremely rapid heating and/or high temperatures, most coal reactions in coal utilizing technologies start with a pyrolysis step [Wen et al., 1979; Lee, 1987; Yun et al., 1991]. Under very high heating rate conditions, pyrolysis and char reaction may occur simultaneously [Smoot et al., 1985]. Moreover, fluidized-bed operation is known to be influenced markedly by pressure and other operating conditions, and thus a detailed understanding of the magnitude of the effects by operating variables is a critical parameter in optimal fluidized-bed reactor design. In order to obtain results on pressure effects, high-pressure thermogravimetric analysis (TGA) system was assembled together with mass spectrometer via a capillary GC column to determine the changes of characteristics in coal pyrolysis that is a first step when coal is introduced into the fluidized-bed reactor.

Among coal utilizing technologies that are currently in the demonstration stage, PFBC (Pressurized Fluidized Bed Combustion) and IGCC (Integrated Gasification Combined Cycle) are most dominant due to their high efficiency and environmentally clean performance. A typical pressure range for IGCC processes is 21-28 bar, while PFBC processes operate under 6-21 bar conditions [Cuenca and Anthony, 1995]. Elevated pressure was known to improve the carbon conversion and coal throughput in the same reactor for IGCC [Azuhata et al., 1986] and PFBC applications. One simulation result demonstrated that pressurizing the fluidized bed to 15 bar for coal combustion at 700 °C yielded 5% increase in carbon conversion efficiency [Song et al., 1996]. Therefore, a fundamental understanding of pyrolysis/combustion/gasification processes is urgently needed for more efficient reactor design. However, because of the lack of instruments that can analyze the weight change or product gas from these high-pressure reactors, only limited data are available in the open literature. Moreover, the available data are mainly related to the final volatiles/char yields without details on the intermediate reaction process.

A recent report [Saastamoinen et al., 1996] reviewed the conflicting results on the pressure effects in combustion rates and pyrolysis yield, in that the effect of pressure on the coal combustion rate in fluidized bed conditions is usually unaffected by the pressure, while in some cases rate increased with pressure. In addition, the unusually increased pyrolysis rate with pressure was reported in one pulverized peat sample in the same report, whereas one report on pulverized wheat straw showed negligible effect of pressure on pyrolysis [Fjellerup et al., 1996]. These observations indicate that more high-pressure experimental data are needed with detailed information on the steps of the process. Increase in pressure under pyrolysis conditions generally decreases the total yield of volatiles [Gibbins et al., 1989; Saastamoinen et al., 1996] that is, the amount of weight loss in TGA systems. Particle temperature decreases with the increase in total pressure [Smith et al., 1994] since the mass transfer or diffusion rate constants are inversely proportional to pressure [Speight, 1994; Song et al., 1996]. When oxygen is involved in the reaction, however, the overall reaction rate increases due to the increased oxygen partial pressure at the high pressures [Speight, 1994].

The objective of the study was to investigate the effects of two different atmospheres, inert and water vapor laden, and two different pressures, 2.7 bar and 35 bar, on thermal decomposition processes of coal. Coals used were the Pittsburgh No. 8 high volatile bituminous coal from the Argonne Premium Sample Bank, Cyprus coal from U.S.A., Drayton bituminous coal from Australia, Chinese Datong bituminous coal, and Alaskan Usibelli subbituminous coal. In addition, effects of low temperature weathering were verified with Usibelli coal.

EXPERIMENTAL

The experimental system consists of a Cahn model TG-151

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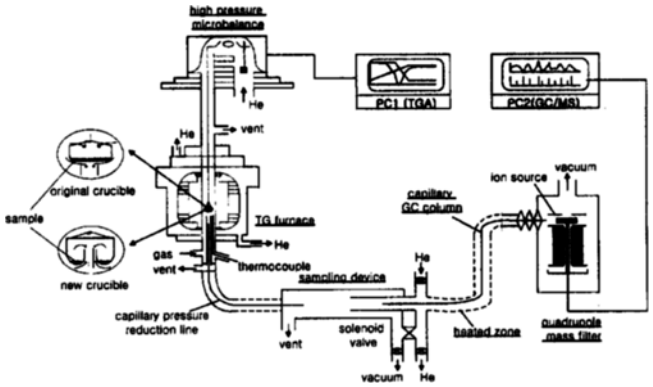

Fig. 1. Schematic diagram of the high pressure thermogravimetric system with on-line gas chromatography/mass spectrometry.

high pressure thermogravimetry instrument, pressure reduction line, vapor sampling inlet, short GC (Gas Chromatography) column, and MS (Mass Spectrometer) detector, as shown in Fig. 1. The TGA (Thermogravimetric Analysis) system was operated at 2.7 bar (25 psig) or 35 bar (500 psig) with a heating rate of 10 °C/min up to a final temperature of 950 or 1,000 °C and with a 10 min isothermal hold at 150 °C to start the water vapor flow. The isothermal hold time of 10 min removed most moisture from coal samples and thus moisture effects were minimized. Furthermore, all thermograms were subtracted with blank run data obtained at the identical heating ramp and flow conditions but only without coal sample. This subtraction procedure is required to eliminate the initial hump that is caused by the buoyancy effect of the sample basket at the low temperature region.

The value of 35 bar was chosen on the basis that the practical application pressure range in IGCC and PFBC could reach 35 bar. The reagent gas was helium with or without added water vapor. Coal sample weights ranged from 66-78 mg of −100 mesh size and, during the operation, the reagent He gas was flowing continuously through the reactor section at 500 ml/min. Steam was added through an electrically heated water chamber and the steam amount was defined as the amount of steam as a weight basis in the flowing total gas flow into the crucible area.

A new crucible design illustrated in the left side of the Fig. 1 was employed in order to maximize the transport yield of pyrolyzates into the capillary column that is connected to the mass spectrometer. The original crucible from the manufacturer is just a simple pan for normal TGA experiments. When the pan-type crucible is used, however, most pyrolysis products are dispersed so that not enough mass is conveyed into the mass spectrometer even though MS detector is a very sensitive device. New crucible design facilitates more concentrated transport of pyrolyzed products into the GC/MS system while not interfering the sensitivity of the weighing balance. Due to the gas flow around the hole in the new crucible design, there exists a gap between the wall of the crucible hole and the capillary column inserted into the crucible. Thus, weighing sensitivity is not sacrificed.

A portion of the produced gas from the TGA system was guided to the 1 m×50 micron i.d. fused silica capillary column, which was employed as a pressure reduction line. An automated vapor-sampling inlet provided a repetitive vapor sampling for the GC column. The sampling inlet was directly connected to a 2 m×150-micron i.d. fused silica capillary GC column coated with methyl silicone. The separated products were detected by an ion trap detector (Finnigan MAT) MS system. Mass scan range in the ion trap detector was 26-300 m/z at 2 scans/sec.

Carbon content of employed coals in daf basis was 70.7% in the American Usibelli subbituminous coal, 74.4% in the Cyprus coal from U.S.A., 79.24% in the Australian Drayton bituminous coal, 79.8% in the Chinese Datong bituminous coal, and 83.2% in the American Pittsburgh No. 8 bituminous coal. Coal rank was expressed as carbon % in daf basis in this study.

Samples of air-exposed/dried coal were prepared from the Usibelli coal after storing under ambient environment of coal silo that was kept from any wetting by rain and from sunlight for eight months and then grinding with 150 °C hot LPG-combustion flue gas flow in the pulverizer. Unoxidized Usibelli coal was prepared only by grinding procedure. Remaining moisture content of both samples was less than 3% which was later removed in the TGA runs through isothermal heating at 150 °C for 10 min. TGA data were normalized based on the weight at 150 °C in order to get rid of effects by moisture. Air-exposed/dried Usibelli coal lost 3.12% weight till 200 °C, while the unoxidized Usibelli sample showed 3.68% weight loss at 200 °C, illustrating that most moisture was removed in TGA data after 200 °C.

RESULTS AND DISCUSSION

Basically, three parameters were focused in the study, which are the magnitude of reactivity variation in inert gas environment for five coal samples as well as in steam-enriched environment for three coal samples and the effect of air-weathering on the reactivity in pyrolysis reaction with pressures upto 35 bar. Since each coal sample contains a different level of mois-

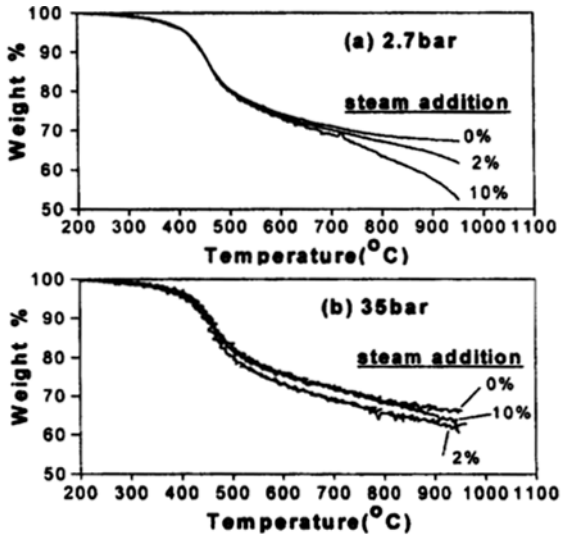

Fig. 2. Effects of pressure and steam addition on the TGA profiles using Chinese Datong coal.

ture and the initial weight reference is dependent upon the dryness of coal, the samples were maintained at 150 °C to be dried for 10 min. Therefore, weight loss change in % was calculated based on the final dried coal weight at 150 °C as 100%.

Fig. 2 illustrates the effects of steam addition on the reactivity at the same operation pressure, in this case using Chinese Datong coal. At low pressure (2.7 bar), the effect of steam on the reactivity becomes greater with increased steam amount after 500 °C region, whereas at the high pressure of 35 bar the effect of steam on the reactivity is relatively minimal with added steam even at the high temperature region. The effect of steam on the TGA profile obtained at the 2.7 bar pressure is profound, especially above 700 °C, with increased steam amount, while the steam effect on the profiles is small at the 35 bar condition. The bigger difference in reactivity above 700 °C appears to originate from the transport limitation of reactants and products that act like a film on the surface of coal powder at the high-pressure conditions. With transport limitation on the particles, reaction rate is being delayed and it looks like the pyrolysis process inside the particle is dominant compared to the effect of steam on the reaction process as a reactant gas. Since steam mainly joins in reactions above 850 °C at 35 bar as illustrated in no-steam, 10%-steam added cases of Fig. 2b, it appears that coal needs to be heated above 850 °C as fast as possible if the reactor is operated at 35 bar. Also, coal needs to be mixed with steam as thoroughly as possible for maximum gasification yield with the same size of gasifier. A little trembling noise in the TGA signals at high pressure stems from the fluctuation of flow by the controlling movement of pressure control valve at the outlet of the TGA system.

Here, one thing should be noted. The TGA results were obtained at a heating rate of 10 °C/min range. However, actual coal conversion processes are operated at a much higher heating rate: 10^4-10^5 K/s in entrained-bed reactors and pulverized coal fired boilers, and 10^2-10^3 K/s range in fluidized bed reactors. Since TGA profiles shift to the high temperature side at higher heating rates, caution should be exercised when applying directly the TGA temperature data that were obtained at low heating rates. Due to the limitation of currently available analytical methods on the very high heating rate conditions like 10^4-10^5 K/s, normally TGA or drop tube furnace (DTF) are employed to obtain the high pressure pyrolysis data. DTF has a limitation of obtaining data during the reaction path, even if not impossible, since only final reacted sample is generally sampled and analyzed. But, DTF has the advantage of reaching the slagging temperature of 1,350-1,600 °C that is for entrained-bed type reactors. Even though the limitation of maximum temperature is 1,000 °C in the normal TGA system, one advantage of applying TGA is getting detailed data during the reaction path, noting that fluidized-bed reactors are operated at the 850-950 °C range. Moreover, earlier vacuum pyrolysis results demonstrate that the distribution and the type of the primary pyrolysis products are largely independent of differences in heating rates of 10^{-2}-10^4 K/s and sample size of 2.5×10^{-5} to 5.0×10^{-2} g range [Yun et al., 1991]. This result indicates that pyrolysis mechanism where heat and mass transfer problems are minimized is rather independent of heating rates. Heating

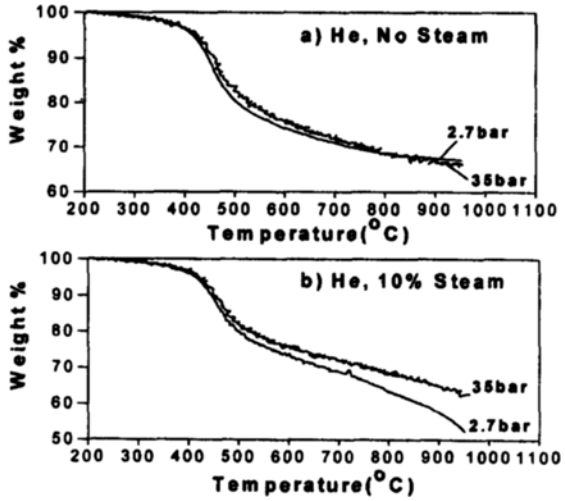

Fig. 3. Effects of pressure under inert He flow with and without steam-added conditions for Chinese Datong coal.

rate in TGA systems ranges from 10^{-2} to 10^1 K/s.

Fig. 3 shows the reshaped profiles from Fig. 2 to distinguish the effect of pressure with and without steam-added conditions. The figure clearly demonstrates the effects of high pressure at the 10% steam-added condition, in that the total devolatilization process is significantly delayed by high-pressure environment probably due to the increased mass transport limitation around the reacting coal particles. Another important observation in the upper figure of Fig. 3 is that the pyrolysis process at 35 bar occurs in a rather wider temperature range for the main pyrolysis reaction than at 2.7 bar in the 400-800 °C range. Wider temperature range means that the weight loss rate (slope of the TGA profile) is smaller at the 35 bar case compared to the 2.7 bar case where the effect is more noticeable around 400-550 °C region. More practical meaning of wider temperature range is that the reaction starts and finishes slower than the narrow TGA profile case. The wider TGA profile corresponds to the lower activation energy in power-law model kinetics, since the logarithmic value of weight loss rate is proportional to the activation energy in the Arrhenius plot and a wider profile means a smaller weight loss rate in the specified temperature range.

For the more reactive subbituminous coal, more dramatic ef-

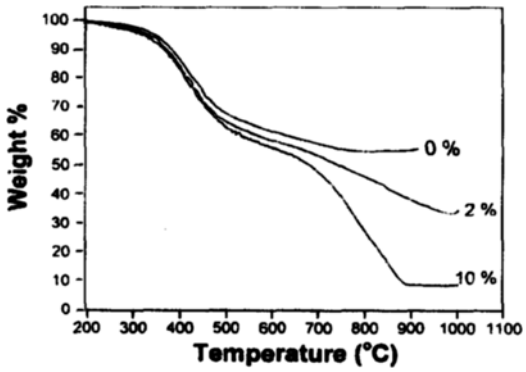

Fig. 4. Effects of steam amount under inert He flow at 2.7 bar for Usibelli sibbituminous coal.

fects by pressure and steam addition can be envisioned. Usibelli subbituminous coal was tested under different steam-added conditions, first at 2.7 bar, and Fig. 4 shows the result. With 10% steam addition at 2.7 bar, all organic components devolatilize after 890 °C yielding only mineral matter, also clearly indicating that steam is reacting with char after 650 °C. In contrast, 56% still remains as char under the condition of no steam addition. When the same 10% steam was supplied, higher pressure of 35 bar resulted in a much delayed pyrolysis profile as shown in Fig. 5, demonstrating that the active char-steam reacting zone is moved into the higher temperature range at high pressure conditions. For the Usibelli subbituminous coal, the remaining 33.6% of weight at 1,000 °C needs more reaction time at 35 bar compared to the 2.7 bar case.

In pyrolysis without oxygen for another two bituminous coals as illustrated in Fig. 6, the process is being delayed significantly with pressure in contrast to the Datong coal case in Fig. 3a where no significant pressure effect was observed. This result demonstrates the importance of coal characteristics even in the same coal rank. In addition, for the Chinese Datong coal and American Pittsburgh coal, pressure effects till 2% steam addition without oxygen seem to be minimal as data show in Fig. 7 for the 2% steam-added condition. However, one result on coal combustion showed that increasing the pressure enhanced the combustion rate [Saastamoinen et al., 1996]. Two aspects need to be discussed here. First, pressure effects on combustion and pyrolysis act in general in opposite way. When there's no oxygen, mass transfer or diffusion rate that is inversely proportional to the pressure appears to play a bigger role resulting in delayed reaction at high pressure conditions. But, oxygen partial pressure increases at the higher pressure yielding higher particle temperatures and thus enhances overall reaction rates in general. Second, pressure effects are quite dependent upon the coal characteristics such that even the same rank coals might exhibit a quite opposite behavior.

Considering that actual IGCC and PFBC processes are operated at high pressure conditions, the above results exhibit the importance of high pressure data and indicate that more residence time would be required to finish the reaction of coal particles in the same size of reactor compared to the residence time estimated based upon the low pressure reaction data for the identical coal sample. It should be emphasized that the comparison of residence time is applicable only when testing the same coal. For different volatiles-containing coals, required residence time is more related to the reactivity of volatiles that is known to be consumed first before the char reaction and thus higher volatiles-containing coals need less residence time in general.

Data on the remaining weight for different rank coals has a significant meaning in the aspect of coal-treating capacity by the same reactor volume. Remaining weight after the reaction by different amount of added steam, as demonstrated in Fig. 7, differs significantly with coal rank. In the case of 2% steam addition, final remaining weight in bituminous coals (79.8%C Datong and 83.2%C Pittsburgh coals) is almost identical even when the pressure is increased to 35 bar. On the other hand, a subbituminous coal (70.7%C Usibelli coal) exhibits a bigger effect by increased pressure, which appears to be caused in part by inherent moisture (about 24%) in the Usibelli coal that acts as its own steam source. Please note that heating at 150 °C for 10 min in the TGA run removes most of the surface moisture, not the inherent moisture that is tightly bound in the coal struc-

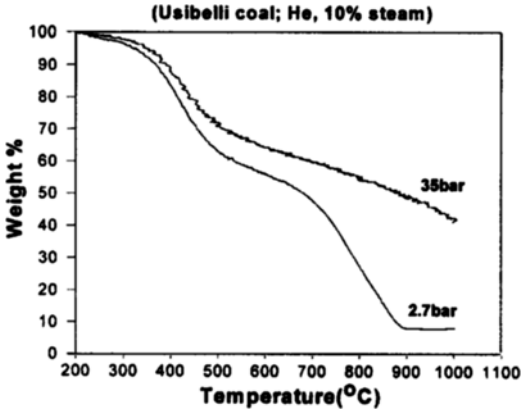

Fig. 5. Effects of pressure under He flow with 10% steam addition for Usibelli subbituminous coal.

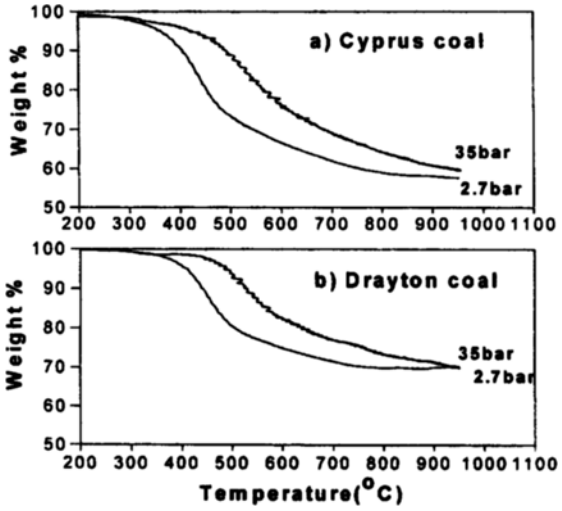

Fig. 6. Effects of pressure under He flow observed in two bituminous coals.

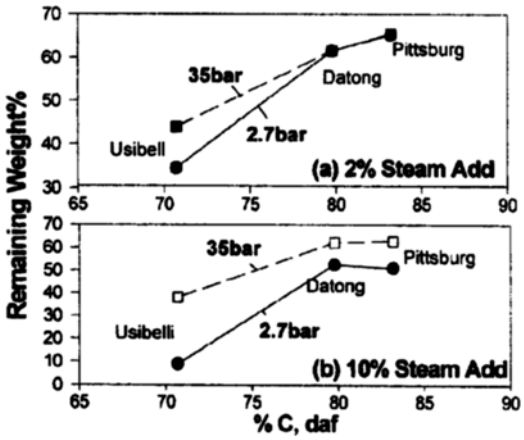

Fig. 7. Remaining weight variation with coal rank at different pressure/steam-addition conditions.

ture. However, when the steam amount is sufficiently supplied like 10% as in the bottom result of Fig. 7, bituminous coals are also influenced noticeably as in the subbituminous coal although the degree of change in remaining weight is smaller in the cases of bituminous coals.

The results in Fig. 7 indicate that pyrolysis reaction is being delayed under high-pressure and 10% steam-added conditions compared to the low-pressure conditions, as exemplified by higher final weight in high pressures, and also those effects of steam addition are rather stronger in a subbituminous coal than in bituminous coals. In other words, the effects of steam are becoming insensitive at high-pressure reactor conditions and are more sensitive in a subbituminous coal rather than in bituminous coals. Furthermore, for the same coal sample, the lowest remaining weight has been observed at the conditions of low operation pressure and high steam supply. With insufficient steam supplied in thermal decomposition, bituminous coals showed a minimal effect by reactor pressure on the remaining weight while more than 10% difference in remaining weight was observed by high pressure operation with a subbituminous coal. With sufficient steam supplied, a subbituminous coal showed more than 30% difference in remaining weight, whereas a mere 10% difference was noticed by pressure effect in bituminous coals. The results till now mainly concentrated on the effects of steam and pressure to the gasification behavior under inert gas environment. In the upcoming years, the effects by hydrogen, CO, and CO_2 are planned to be investigated.

Moreover, the air-weathered subbituminous coal exhibits a less sensitive response to temperature compared to the unoxidized fresh coal sample, as illustrated in Fig. 8. The results suggest that even air oxidation at room temperature for a prolonged time can cause markedly different pyrolysis characteris-

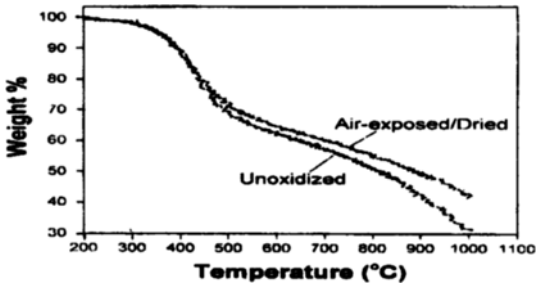

Fig. 8. Effect of low temperature weathering on the thermal decomposition process, using Usibelli subbituminous coal (He, 35 bar, 10% steam).

tics at high pressure, especially in the reactive low rank coals like a Usibelli subbituminous coal. The mechanism of low temperature air oxidation is known to proceed through the formation of carbonyl groups from aliphatic bridges in coal [Joseph and Mahajan, 1991]. As described in the experimental section, both samples were dried by subjecting at 150 °C for 10 min in order to minimize the moisture effects on the pyrolysis. Pyrolysis exhibits significant difference when water or steam exist, but the presence of moisture does not present a noticeable effect on the rate of low temperature oxidation of coal [Speight, 1994].

Fig. 9 shows one example of GC/MS analysis on the effluents from TGA for Usibelli coal. At low pressure of 2.7 bar, pyrolyzates clearly are produced at two distinct humps as shown in total ion profiles containing many kinds of aliphatic components. But, at the pressure of 35 bar, two humps observed in low-pressure pyrolysis are rather combined together. In the figure of total ion profile, scan number is directly proportional to the temperature because the analysis was done at the constant heat-

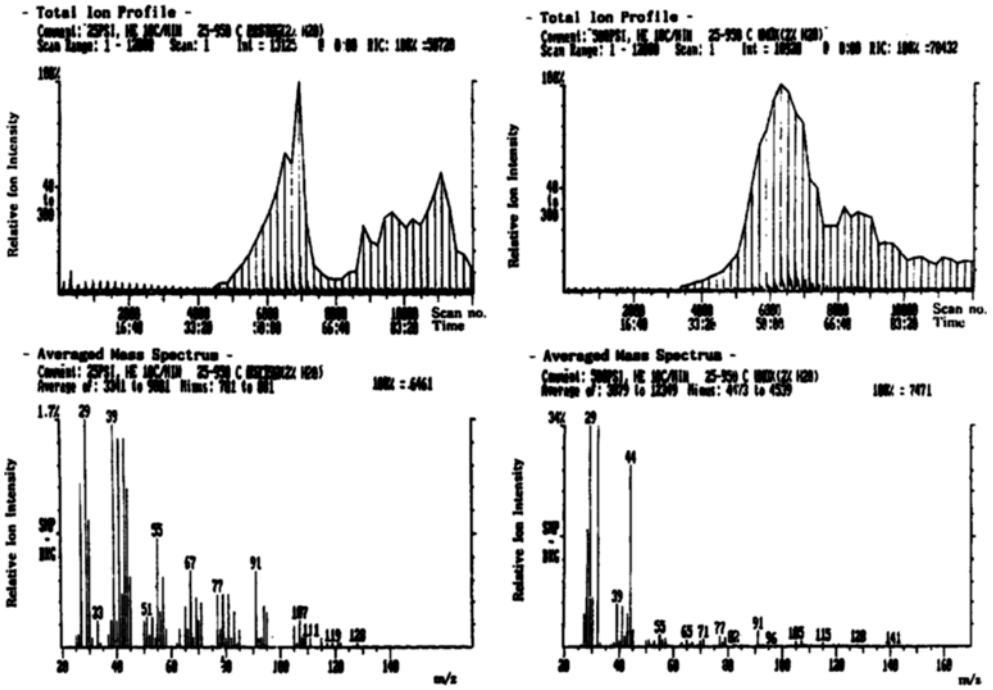

Fig. 9. Total ion profiles and averaged mass spectra obtained at different pressure conditions (Left: 2.7 bar, 2% steam, Right: 35 bar, 2% steam).

ing rate (10 °C/min). The important point here is that pyrolyzates normally have a very reactive tendency when produced and, if reactive components are emerged at the same time as in the high-pressure case, they tend to bind together resulting into coke-like structure. From the viewpoint of molecular level, this kind of detailed characterization at the actual process pressure condition might provide more fundamental information for improved reactor design in the long run.

CONCLUSIONS

A high pressure TG/GC/MS system was designed to offer minimal transport resistance to large and/or polar reaction products and to facilitate removal of condensed tar fractions. A special crucible design promotes rapid removal of reaction products from the reaction zone inside the TGA system. The TG/GC/MS system demonstrates the feasibility of on-line GC/MS monitoring of conversion reactions in high temperature/high pressure reaction environments. From the high pressure TGA experiments, the following conclusions were made:

(1) Coal tends to exhibit a multistage degradation behavior with low temperature desorption processes being followed by bulk pyrolysis phenomena and, finally, char reactions.

(2) Pyrolysis process at high pressure occurs slowly compared to lower pressure cases. Thus, reactor design based on data from low-pressure results might lead insufficient reaction at the actual high-pressure operation.

(3) Effects of steam are less significant in high-pressure conditions, and the magnitude of steam-addition/pressure effects is bigger in a subbituminous rank coal than in bituminous coals.

(4) Low temperature weathered coal exhibits fewer effects by reaction pressure in steam-laden reaction and thus might require more reaction time in the same size of the reactor.

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