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THE CANMET COAL HYDROPYROLYSIS PROJECT

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NOVEMBER 1984

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## ABSTRACT.

Pyrolysis and hydropyrolysis are relatively simple methods whereby liquid hydrocarbons may be produced from coal. In order to study these processes on a 1 kg/h scale. CANMET has had constructed a flash hydropyrolysis unit at Ontario Research Foundation. Mississauga. The equipment has been used in a short preliminary series of experiments on the hydropyrolysis of Forestburg subbituminous coal. Results from these experiments are discussed, along with plans for future use of the unit.

* Denotes speaker.

Introduction.

Coal pyrolysis has been used for many years for the production of burnable gas, hydrocarbon liquids and coke. More recently, much interest has been shown in rapid or "flash" pyrolysis of coals both in inert atmospheres and in hydrogen. The latter process is usually known as hydropyrolysis. The influence of heating rate on the quantity and quality of products from coal pyrolysis was studied in small scale apparatus by Squires et al. (1,2) who used U.S. coals, and by Stangeby and Sears in a similar study of Canadian coals (3,4).

The major reason for the slowness in development of flash hyropyrolysis of coal is probably the hydrogen pressure required to achieve worthwhile improvement over straight pyrolysis. A minimum of about 7 MPa hydrogen pressure has been found to be necessary, and this considerably complicates the engineering problems in developing a commercial scale process. However, if hydropyrolysis can provide a sufficiently attractive product slate, then it will be of interest.

Coal flash pyrolysis processes have been developed up to commercial scale, most notably by Lurgi in Germany and by Occidental and Tosco in the U.S.A.. Both the Lurgi and Occidental processes use spent char as the heat carrier for pyrolysis of fresh coal, while in the Tosco "Toscoal" process ceramic balls are used. Yields of volatile material from the coal fed to these processes significantly exceed those expected from Fisher assays. All these processes are quite usable, but interest in their application has waned considerably with the fall in oil prices in the early part of this decade. This situation is unlikely to be permanent though. and when oil prices rise again interest in this type of process is likely to be renewed.

Hydropyrolysis is very much less developed, and work has so far been restricted to relatively small scale equipment. Amounts of coal fed are now of the order of a few kilograms per hour, which falls far short of commercial scale operation. In the U.S.A.. Rockwell International, Cities Service Co. and Brookhaven National Laboratory have all worked on about this scale for some years. but similar studies in Canada are only just beginning. Both CANMET and the Alberta Research Council now have equipment similar in basic desiqn to that at the Brookhaven National Laboratory.

The CANMET hydropyrolysis project was begun in 1980 when Kilborn Ltd. of Toronto undertook a contract which involved the construction of a 1 kg/h coal flash hydropyrolysis unit. This unit is now complete and is being operated under contract by Ontario Research Foundation personnel at the premises of O.R.F. in Mississauga

A preliminary series of hydropyrolysis experiments using Forestburg subbituminous coal has been carried out, and in the light of results from these experiments, procedures for operation of the unit and analysis of the products are being revised in preparation for further work which will begin shortly.

## Objectives

The primary objective of the programme is to investigate the processing of Canadian coals in this type of unit. The long term goal is to develop a process which could be used to "skim off" high value liquid fuels from coals which are destined for combustion. The opportunity to use a significant fraction of a bituminous coal as liquid fuel or chemical feedstock is now lost when the raw coal is burnt in its entirety. Achievement of this objective is also dependent on the demonstration of reliable burning in a furnace of the char resulting from the pyrolysis or hydropyrolysis process.

## The CANMET Flash Hydropyrolysis Unit

The CANMET flash hydropyrolysis unit is based on a heated vertical tubular reactor at the top of which finely divided coal enters and meets preheated hydrogen. Both the coal and the gas flow downwards in the reactor, and at the bottom any solid material falls into a collecting chamber, while gases and vapours pass into a series of condensers. The coal particles in the reactor are in free fall. Figure 1 shows a flow diagram of the unit

Hydrogen is supplied from cylinders at 6000 psig, and led through pressure and flow regulators into a preheater. Originally, a compressor was built into the system to permit purchase of hydrogen in regular cylinders. However, it proved more practical to use hydrogen which is supplied at high pressure. A helium supply is available for flushing the system.

The gas preheater is of the direct resistance type, where a large current is passed through the tube carrying the gas. In the unit as originally constructed, the tube was heated by a conventional oven, but this proved ineffective and was replaced. The direct resistance method requires the use of an electrical isolator in the line upstream of the heater.

Coal is stored in a pressurised hopper at the top of the reactor tube, and is fed to the reactor by a motor driven worm feeder at the bottom of the hopper. The rate at which the coal is supplied by this feeder is not as stable as was hoped. and this part of the system is being reconstructed. The bottom section of the hopper system is water cooled to avoid excessive heating of the coal.

Coal fed into the reactor meets the hot hydrogen and flows with it down the reactor. This reactor has an I.D. of 32 mm and a length of 3.7 m. Four ovens maintain the temperature of the top part of the reactor at the required value. which is usually the same as the inlet gas temperature. The lower part of the reactor is not heated, and if necessary may be cooled by passing cold gas through another tube coiled about it. This section of the reactor is used to lower the temperature of the reactants and thus quench the reaction. At intervals down the reactor tube are sample ports to permit sampling of the gas stream at intermediate stages in the reaction. This facility has not been used as yet.

At the bottom of the reactor the char trap collects solid

material and the gaseous stream passes into a series of two condensers. The first of these is water cooled and the second is maintained at -70°C by a liquid nitrogen cooling system. These condensers are vertical tubes through which the gases flow from top to bottom, and condensed liquids are collected in traps at the bottoms of each. The remaining gas is vented through a pressure control system and a meter. Samples are taken for analysis.

Because of the dangers involved in the use of high temperatures and high pressure hydrogen, the unit is equipped with an emergency dump valve. through which the gas may rapidly be vented to the outside. The unit is enclosed in a room which is closed to everyone while a run is in progress. and which is equipped with hydrogen sensors to detect leaks and a ventilation system to remove any hydrogen which does escape.

Operation

After the inevitable commissioning problems the unit is now operating smoothly. In spite of the high pressure of gas involved only one point in the system caused significant sealing problems. This was the junction between the low temperature condenser and its collection trap. On several occasions this junction leaked and subsequently reclosed, leaving no trace of the source of the problem. It was finally realised that this part of the system must be fully cooled before high pressure was applied, to avoid leaks caused by differential contraction of the junction.

In normal operation the feed hopper is loaded with coal, the unit is sealed and then pressurised with helium at 14 MPa. A check is made for leaks, and any that are found are rectified. With a slow flow of helium through the system, the reactor ovens are switched on and the reactor brought up to operating temperature. As the preheater has a very small thermal mass, it is not necessary to switch it on until a few minutes before the start of the run.

When the reactor temperature is near the value required, the helium flow is replaced by hydrogen at the desired flowrate, and the gas preheater is switched on. The temperatures of the reactor and preheater are then allowed to equilibrate while the hydrogen clears the helium from the system. When the situation is stable the coal feeder is switched on

Two methods of measuring the gas flow are used: the pressure in the hydrogen cylinders and the correspomding time are recorded at approximately six-minute intervals during the run. and the quantity of effluent gas which has left the system is simultaneously noted. A run is defined as the period from the beginning of feed of coal to the end of feed. A mass flowmeter was also included in the hydrogen supply system, but this has so far proven unsatisfactory

Several samples of effluent gas are taken during the run, but no other product can be collected until the run has ended and

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the equipment has cooled. The high pressure must be released quite slowly to avoid the loss of volatile material with the gas remaining in the system after the run.

Solid and liquid products are collected and weighed. Analysis of the solid char in the trap at the bottom of the reactor is straightforward, but the liquid in the first condenser trap contains two phases which sometimes tend to form an emulsion. This is not easy to separate. One phase is basically water and the second is a dark foul-smelling liquid which constitutes the bulk of the hydrocarbon liquid product. The second condenser trap contains a much lighter organic liquid phase without any significant amount of water. The main constituents of this are benzene, toluene and xylenes


Results and Discussion

To date, a total of fifteen successful runs have been carried out in the unit. Five of these were the commissioning runs immediately following completion of the unit, and the rest were part of a preliminary contract for its operation. The amount of information gained from each run increased as experience was gained. The primary purpose of the commissioning runs was to achieve acceptable mass balance for the process, so little analytical information was recorded for these. For some of the preliminary contract runs- separation of the water and organic phases from the first trap was not achieved, so the amounts of water and heavy organic material remain unknown. The amounts of lighter aromatic compounds were determined.

Once the type and grind of coal to be used has been decided, four independent variables may be chosen for each run. These are coal feed rate, gas feed rate, pressure and temperature. It is also possible to use different temperatures in different parts of the system, e g. preheater and main oven. but results from this type of run are of less interest. The residence time of a coal particle in the reactor is dependent on the other variables. An estimate of this may be calculated.

Series of runs were carried out, in each of which only one of the major variables was altered. Of these variables, temperature and pressure could be controlled most accurately. The hydrogen flowrate was set to a value which was calculated to give the desired particle residence time. and the coal feeder motor was driven at a speed which was expected to give the required feed rate. The actual rate could be measured after the event with a fair degree of accuracy. but setting it was only approximate.

The coal used in these experiments was Forestburg subbituminous. Its analysis and particle size distribution are given in Table 1.

Figure 2 shows the percentage weight loss of the coal on passage through the unit, as a function of temperature in the range 490 to 800°C. Results from experiments carried out at 1000, 1250, 1500 and 1750 psig are shown. The data from experiments at 1000 psig show a smooth curve rising from 15% at 490°C to an apparent maximum of approximately 50% at about 800°C. The effect

of higher hydrogen pressure is clearly to increase the weight lost, but it may be seen that the effect is not large and that the data do not permit a detailed assessment of the effect. No account is taken here of the differing coal or hydrogen feedrates used in these experiments.

Figure 3 shows the percentage of carbon in the original coal which was detected as hydrocarbons in the gas product. This shows that conversion of the coal carbon to gas increases both with temperature and with hydrogen pressure. The dependence on pressure is shown more clearly in Fig 4, where the data for 800°C are plotted against pressure

Significant amounts of carbon are converted to carbon oxides, which also appear in the gas analyses. The total amounts of carbon converted to the oxides are shown in Fig 5. Here it is clear that this parameter has no very strong relationship with either temperature or pressure in the 700 to 800°C range. At 490°C the amount of reaction was so small that virtually no gaseous products were detected.

Yields of benzene, toluene and xylenes were measured for ten runs. These data are plotted against temperature in Fig 6. The scatter in this diagram is quite bad, possibly because of the effects of variations in the flowrates of gas and coal, both of which are not being taken into consideration. Nevertheless it appears that the yields of BTX are increased by increased pressure and temperature in this range Significant quantities of naphthalene are also produced, as much as 2% of the coal carbon being converted to this material

Products which were not adequately separated in this initial study were water and heavy hydrocarbons. From the four runs in which a separation was achieved, indications are that the amount of heavier liquid organic material was from about one to three times the amount of BTX. Separation and analysis of this material is the first objective of the next series of experiments.

The amount of hydrogen in the inlet gas stream is much larger than the amount which reacts with the coal, so the difference between the hydrogen flows in the inlet and outlet streams is relatively small. This makes determination of the overall mass balance for the process somewhat difficult. However, the amount of hydrogen is much smaller than the amounts of other elements, so errors in the hydrogen data are relatively unimportant. The mass of products recovered lies in most cases in the range 95% to 102% of coal reacted. Since some hydrogen has been added, it is clear that product material is being lost, but this is not a very large amount, and the results are quite consistent. There are some indications that the problem is a loss of volatile liquids during system shutdown. and it is hoped that this can be rectified in the next experimental programme.

Samples of char resulting from three of the runs were sent for petrographic analysis, with a sample of the original coal for comparison. These runs were carried out using identical hydrogen and coal feedrates and the same hydrogen pressure (1000 psig). The only variable was the temperature, which was 650, 750 and 800°C for the three runs.

Results from the petrographic analyses indicated that the maceral structures of the particles had been completely changed,

and that there was no "unaltered coal" at all. This indicates that the particles had been heated throughout during their passage through the reactor. The small amounts of liptinite and inertinite present in the coal had been completely destroyed, leaving just the huminite macerals. The huminite macerals were converted to vesicular material, which was classified at the analysing laboratory into "vesicular" and "highly vesicular" categories. It was noted that the proportion of the latter rose markedly with reaction temperature. Reflectance measurements showed that the mean reflectance of the coal rose on hydropyrolysis and rose further with increasing temperature.

The residence time of a coal particle in the reactor depends on all the reaction conditions except coal feedrate. A figure can be calculated for a particle of any given diameter by assuming free fall in the moving gas in the reactor. However, the coal used in these experiments was not of completely uniform size, and the smaller particles have longer residence times. which results in more complete reaction for them. Particle size analysis on the coal and chars indicates that the smaller particles do indeed lose more material than do the large ones, thus becoming still smaller and slower falling. This situation can result in complete disappearance of the smallest. Care is required in the interpretation of calculated particle residence times.

Conclusions

The CANMET hydropyrolysis unit has shown itself to be a reliable piece of equipment which is quite straightforward to operate. Problems remain to be solved, the major ones being product recovery and workup, but the unit may now be run on a routine basis. The results obtained so far are consistent with those from earlier small-scale work and show that quite substantial yields of liquid products can be obtained. It is important now to develop methods whereby the heavier liquid products may be characterised, and then to optimise production of useful liquid while minimising the amount of hydrogen which is used in the formation of gaseous hydrocarbons.

High volatile bituminous coals will be processed in the unit, as these may be expected to provide the best yields of liquid products. This will require solutions to the problem of caking which can easily occur with these coals.

Finally, if conditions can be found which provide a good product slate, it will be necessary to develop a process for the hydropyrolysis of larger quantities of coal. This will present new difficulties. a major one being the transfer of heat to reactants in a large reactor vessel. This stage of development is as yet some way off.
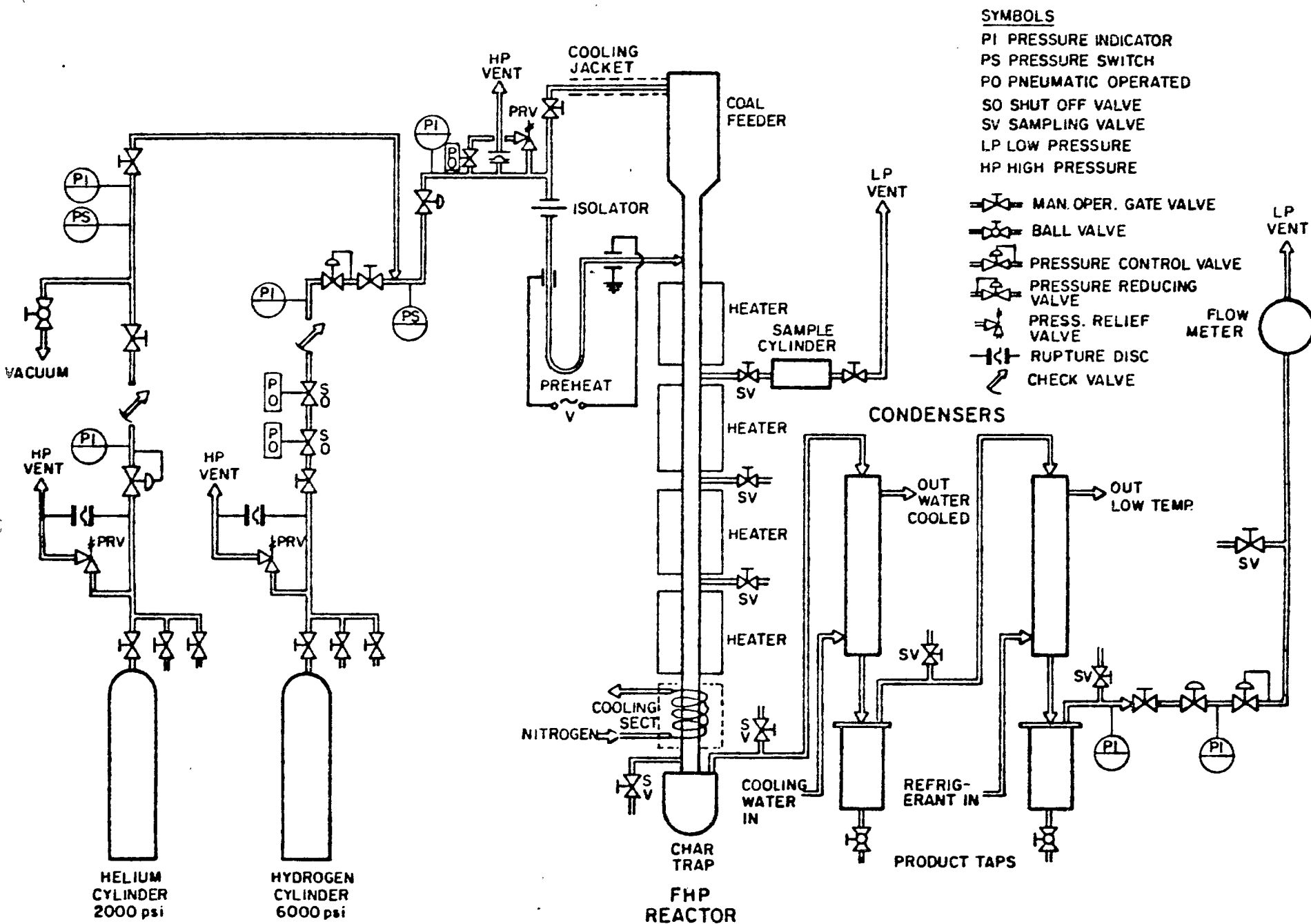
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2. Graff, R A.. Dobner, S  and Squires. A.M.. Euel, 55: 109; 1976.
3. Stangeby, P.C. and Sears. P.L., Fuel, 60; 131; 1981.
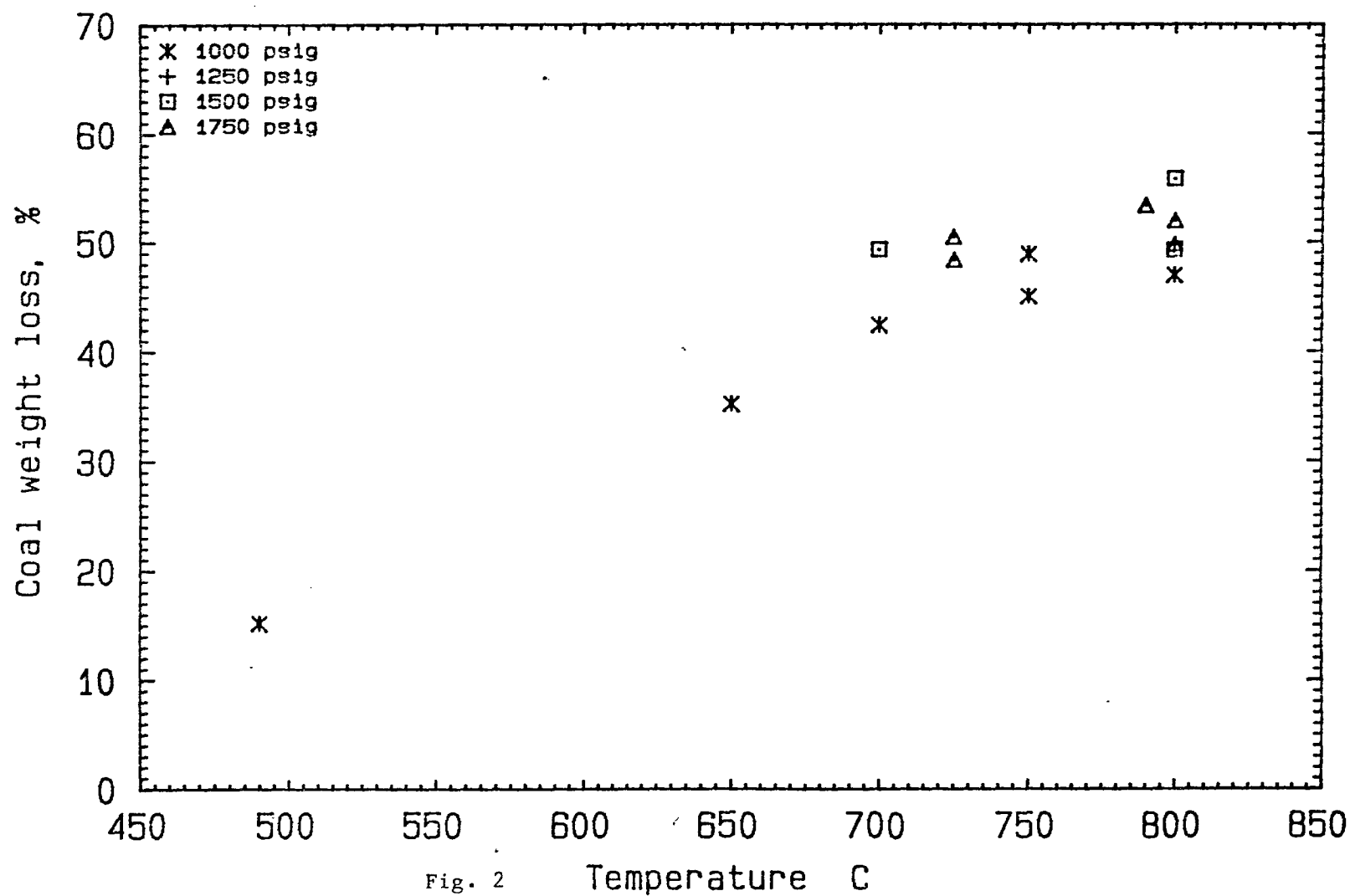4. Stangeby. P.C. and Sears, P.L.. CANMET Contract No. OSU76-00204;  1976.

Table 1 -  Coal Analysis.


| Component | Weight per cent | |
|---|---|---|
| Fixed carbon | 48.14 | mf |
| Volatiles | 39.87 | mf |
| Ash | 11.99 | mf |
| Moisture | 2.36 | |
| Carbon | 67.96 | maf |
| Hydrogen | 4.91 | maf |
| Oxygen | 25.69 | maf |
| Nitrogen | 1.19 | maf |
| Sulphur | 0.25 | maf |


| Size range ($\mu$m) | Weight per cent |
|---|---|
| >297 | 3.7 |
| 210-297 | 24.5 |
| 177-210 | 32.2 |
| 149-177 | 15.8 |
| 105-149 | 18 8 |
| <105 | 4.9 |

Fig. 1   CANMET and ONTARIO RESEARCH FOUNDATION
PROCESS FLOW DIAGRAM — FLASH HYDROPYROLYSIS PILOT UNIT

Coal weight loss,
temperature dependence.

Fig. 2    Temperature  C

# Coal carbon converted to hydrocarbon gas, temperature dependence.
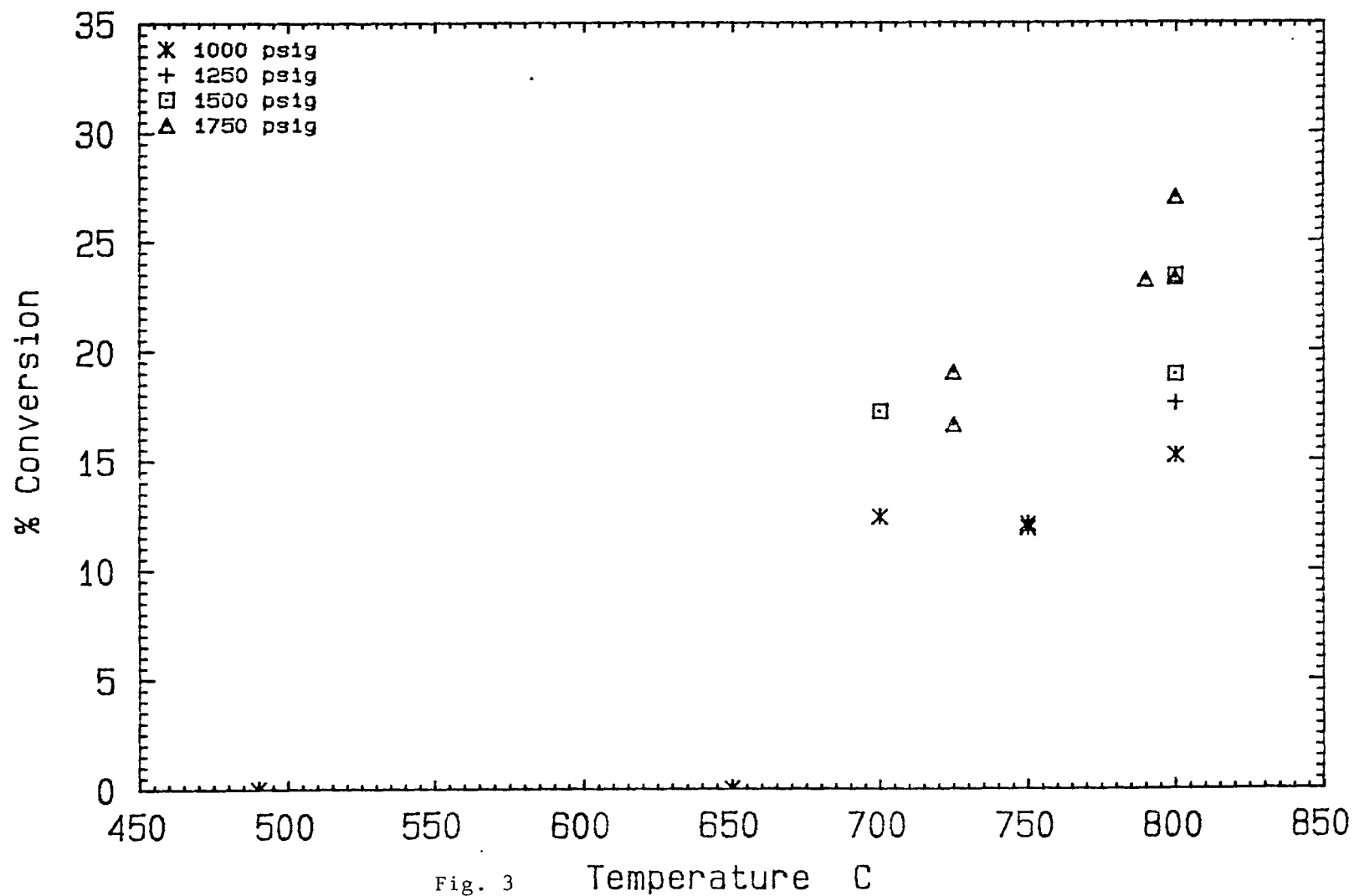


Fig. 3   Temperature  C

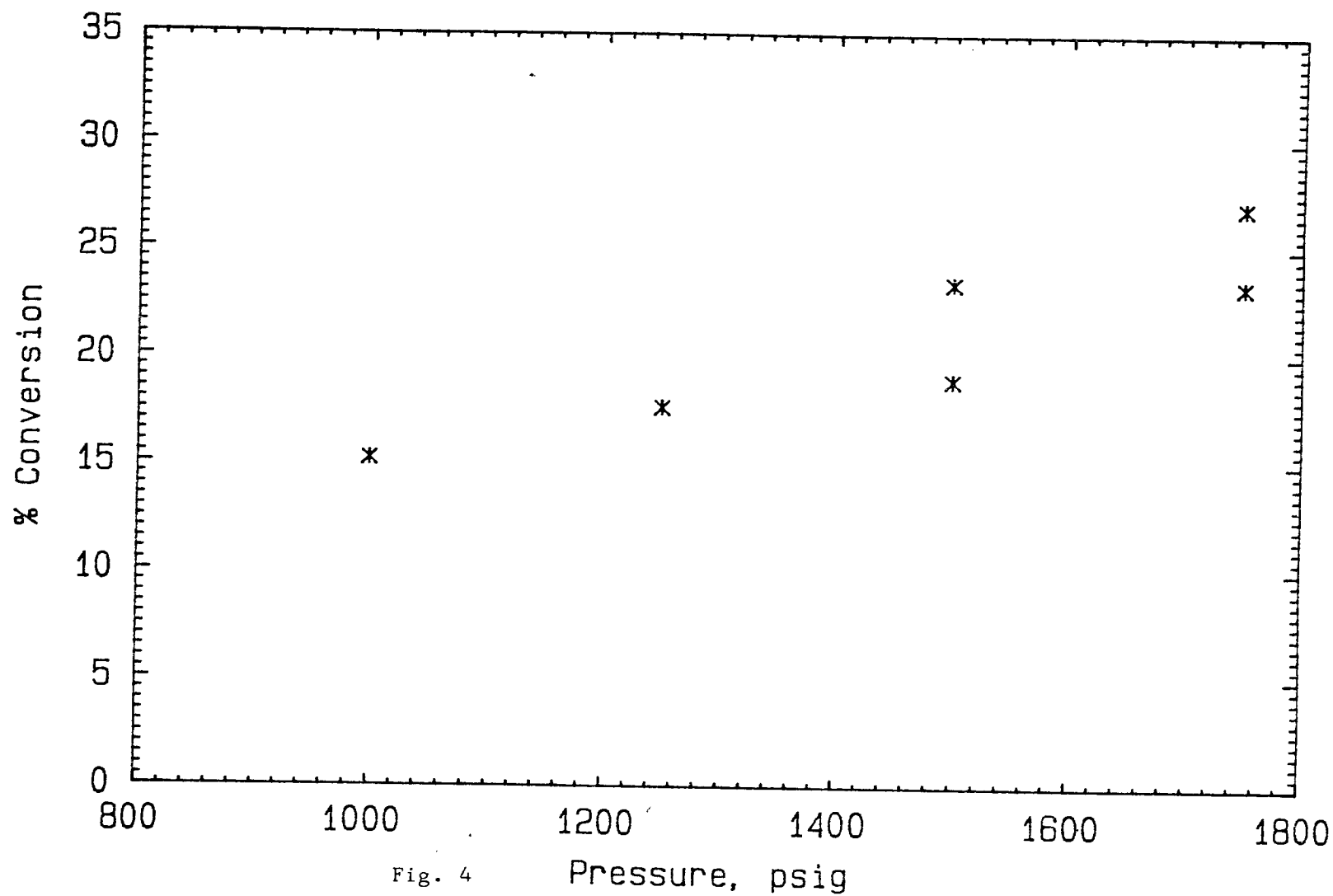Coal carbon converted to hydrocarbon gas, pressure dependence at 800 C.

Fig. 4    Pressure, psig

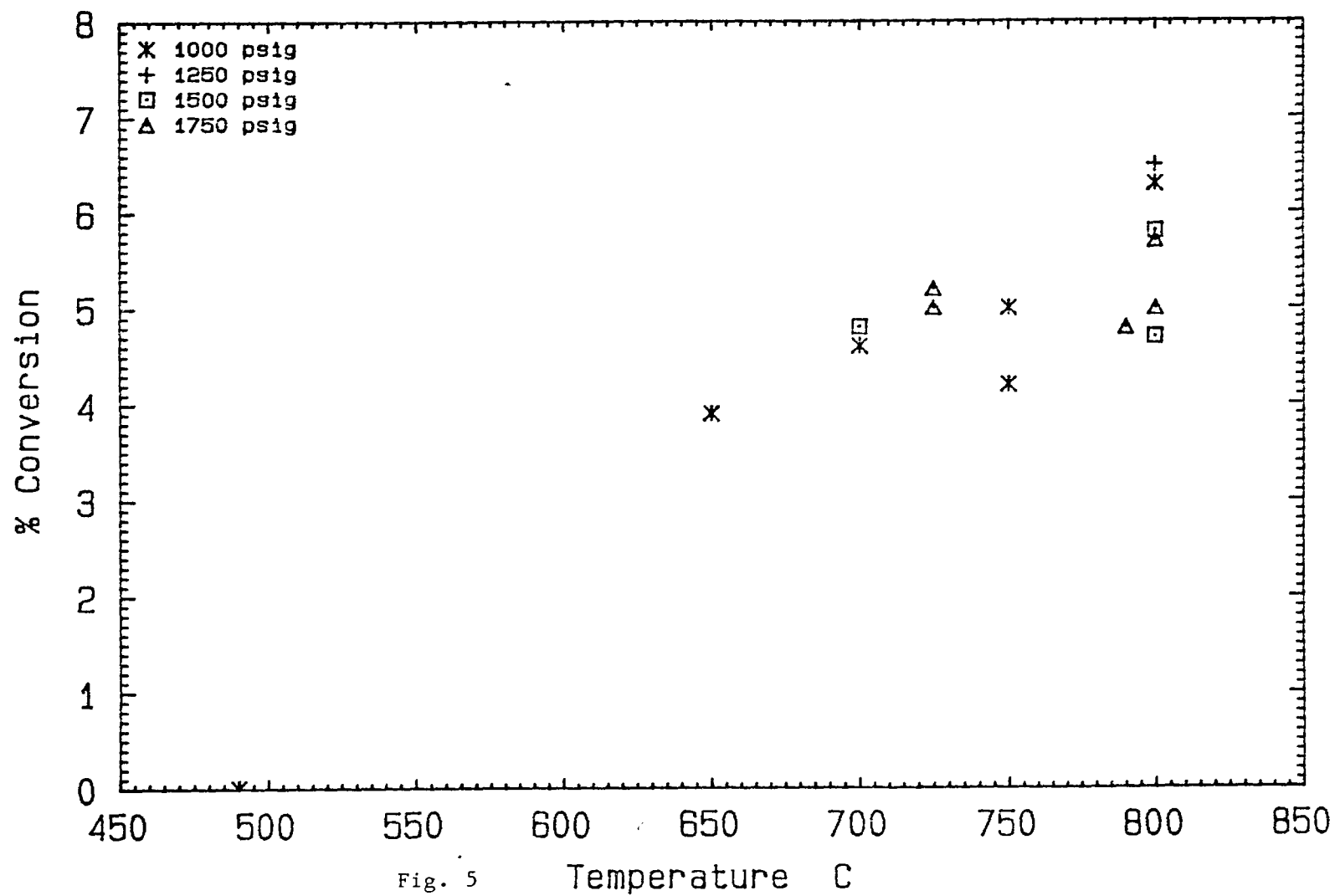Coal carbon converted to CO and $CO_2$. temperature dependence.

Fig. 5 Temperature C

Coal carbon converted to BTX, temperature dependence.

Fig. 6    Temperature   C