

CHARACTERIZATION OF COAL BY PYROLYSIS

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1. Introduction

Coal characterization is an old subject. The heating value is a major important figure from an economic point of view. The common classification in ranks, however, has been associated with the coking properties and is usually based on the volatile matter content. Its value for the firing (and gasification) of coals is limited. One indirect method - vitrinite reflection is based on petrographic correlation. Also DTA and TG measurements are studied, but have not gained much use as yet.

The annual report 88/89 of IEA Coal Research gives some comments on the matter, stating that characterization should identify properties, that are critical to the performance of the coal. There is a need for better evaluative tests, based on modern techniques, but it is considered unlikely that methods can be devised in the near future, which are both specific, good for all coals and still simple.

Considering these methods and other characterization measurements, which are mainly analytical, it may be stated, that no method does really try to relate measured properties of coal with its burning characteristics, except for the somewhat primitive "drop-tube burning". Studies of the behaviour of coal particles in flames - usually contrived as some pyrolysis/gasification model - can be considered as characterization but may not easily produce figures for inherent coal properties.

The suggested approach, presented here, emphasizes pyrolytic properties of coal. A small sample is subject to a rapid well controlled laser-induced pyrolysis, followed by an equally controlled gasification, using a microbalance, to estimate the reactivity of the char, formed by the pyrolysis. The principal aim is not to contribute to the fundamental understanding of coal burning but to add - by the use of advanced equipment - to the empirical comprehension of burning properties of coal.

The purpose of the proposed measurements is thus related to the pyrolysis and gasification, which occurs during practical firing, where the time and intensity of pyrolysis may vary considerably between coal particles. The way a particle responds to pyrolysis is known to influence the char reactivity and may thereby determine the final burning (gasification). The approach presented here is apparently not attempted before.

The use of a very small sample is necessary to achieve a rapid pyrolysis with a laser beam, which in turn necessitates the use of a microbalance for the gasification step.

2. Equipment and procedure

Sample preparation

Coal powder (< 270 mesh) is pressed to a thin disc (< 0.1 mm) and cut to a circular specimen (4.5 mm), which is laid in a tiny quartz glass crucible and its weight recorded. It was established experi-

mentally, that the thickness of the specimen must be restricted to a maximum thickness of about 1 mg.

Rapid pyrolysis

The sample crucible is placed in a pyrolysis chamber (Fig. 1), which is flushed with pyrolysis atmosphere (usually He), and possibly pressurized. A glass window allows radiation of the sample with a laser beam, and a portion of the resulting gas may be sampled through a rubber septum, using a syringe.

A Neodym/YAG laser has been used, giving a beam, coaxial with sample and having the same width. The beam energy could be increased up to 14 J and given 1 to 20 ms duration. The pyrolysis gas was analyzed in a Perkin Elmer 8500 gaschromatograph with double detectors, combined to monitor for H_2 , CO, CH_4 (conjunct), C_2H_2 , C_2H_4 , C_2H_6 and C_3H_6 .

About 90% of the tar formed did deposit on the crucible wall, but no attempt was made to analyze or characterize this product. It would have been a difficult undertaking as such and could not be accommodated in the project.

Reactivity rating

The char disc (about 1 mg) from pyrolysis can easily be transferred to a clean crucible. It is vital that this crucible is handled carefully to avoid any generation of static electricity. The char is covered with a thin layer of quartz wool to assure that no char (or ash) is lost.

The gasification is made in a (locally built) apparatus, seen in Fig. 2, which is for the most part selfexplaining. A Satorius electronic ultramicrobalance (type 4436 MP8) has been used. It is important that the filament (steel + Pt), which carries the char crucible, is centered to avoid any contact to the furnace wall. It is also important to avoid any movement of the balance, when the hanging furnace is heated, which explains the use of an expansion joint. A small stream of nitrogen is used to protect the balance and to keep an unchanged atmosphere around the counterweight.

A partly perforated mixing section at the furnace top protects the filament and gives complete mixing of the two gas streams. Temperatures up to 950°C for H_2O or CO_2 could be used but most experiments were run (with O_2/Ne) at about 430°C. The temperature variation in the furnace chamber could be kept within 1°C.

After insertion of quartz crucible, the gasification is started with extended flushing of the furnace with N_2 before turning on the heating. The temperature rise was normally quite rapid, but not until after about 2 hrs. the temperature became stable and the reactant gas could be admitted. The gasification media (O_2 , H_2O , CO_2) were diluted with N_2 .

During the introductory phase of the experiments it was found to be proper to normalize the amount of char gasified at any time to the maximum amount possible. This latter value was found by raising the temperature of the oven 200°C in a flow of nitrogen, whereafter the oxidation is completed within few minutes to constant weight giving the ash figure.

3. Experimental results

Of the introductory/guiding experiments only a few need to be reported. Reproducibility of the two-step procedure was found to be quite satisfactory. The rate of gasification did not change when the flow of reactant gas was reduced to half, and the rate seems to be directly proportional to the O_2 concentration (25 and 50%). Rate values at comparable conditions in the temperature range 408–438°C gave activation energies in the region 120–150 $\text{kJ}\cdot\text{mol}^{-1}$, indicating that reaction rate only is rate-controlling.

A comparison of the relative rating of two coal samples is shown in Figures 3 to 5, using O_2 (65%), H_2O (29%) and CO_2 (50%). When the differences in curve heights are compared at the same degrees of gasification, the H_2O and CO_2 ratings are nearly the same, while the "separation" is somewhat larger for O_2 . H_2O is, however, more reactive than CO_2 . The use of O_2 is preferred, since the lower temperature is lenient to the furnace.

Using one coal sample, the influence of pyrolysis time at the same laser energy input (12 J) on rate of gasification was measured (Fig. 6). While the amount of pyrolysis residue (char) did not vary much, it is evident, that the reactivity of the char gets considerably higher, when pyrolysis time is short. This effect is likely to increase the spread of burning times in a PF flame.

The effect of laser energy input at constant pulse length (1 ms) was also studied. As seen in Fig. 7 the samples with the smallest amount of energy start at a lower degree of pyrolysis but are somewhat more reactive, why the final level of gasification gets to be more or less the same.

In another study with a set pulse time the ratio of energy to specimen weight was kept constant (Fig. 8). It resulted in almost identical gasification curves.

The composition of the pyrolysis gas varies somewhat with the laser-pulse duration as shown in fig. 7. These values may not be important for combustion performance but could give an indication of pyrolysis properties. When the level of laser energy was varied at constant pulse length the following relative amounts (μl) were formed:

Energy, J	1	2	5	10
H_2	32	88	122	139
CO	9	31	57	81
CH_4	1.2	1.4	1.7	2.3
C_2H_4	0.43	0.46	0.73	1.15
C_2H_2	1.9	5.5	19.6	3.6

The rise in amounts was particularly strong in the lowest range of energy increase, except for C_2H_2 .

From the curves shown so far and several others it can be inferred, that the (relative) amount of "post-pyrolysis" is proportional to the reactivity of the char, expressed as the initial slope of gasification curve.

In the Figures 10 to 13 some pyrolysis and gasification curves are given for the following 4 coal samples within the same rank, the figures being in %:

Origin	H ₂ O	Ash	Volatiles
Australia	2.2	16.1	37.3
Mozambique	2.8	10.1	40.0
South Africa	2.9	13.3	29.9
Poland	2.6	17.2	38.4

It may be stated generally from the "reactivity curves", that the new type of characterization does discriminate between different coals. The differences appear as ultimate levels of (normalized) residue and as response at changes in pyrolysis parameters. It would be of interest to understand how these differences may be explained, but the important matter is to relate the observations to the performance of the coals in practical burning.

Fig. 13 also illustrates the deviation in behaviour, when the pyrolysis is done by heating the coal specimen slowly in the gasification oven. Evidently the slow carbonization yields a reactive char, which has almost the same "gasification profile" as the char from a low energy laser pulse (1 J) of short duration (1 ms). However, in characterization laser pyrolysis is more realistic and easier to control.

Though the use of CO₂ as gasification medium is less attractive, it is of fundamental interest to check the influence of characterization parameters in comparison to O₂. It was found as a main observation, that the difference in reactivity, resulting from short and long pulse lengths, seems to be considerably smaller on CO₂ gasification.

Several experiments were made with different atmospheres and increased pressures in the pyrolysis chamber. On the whole, the effects observed were rather insignificant. Also a splitting of the laser energy into several consecutive pulses seems to give additional information of interest. *Title*

A few experiments with particles of different ranges in the coal powder, used to press the disc specimen, indicate some differences in the reactivity of the produced chars. Evidently, the particle size distribution should be controlled in accurate work.

Finally two series of "characterization experiments" were carried out, one with coals of different ranks, the other a comparison with results, produced by the Danish service and research institute dkTEKNIK.

The first series comprised one subbituminous coal (West Canada), two bituminous coals (South Africa), one "in between" these ranks (Columbia) and, as the last, anthracite. The laser energy was kept constant while two pulse lengths (1 and 20 ms) was used. The results are shown in Figures 14 and 15. The 1 ms experiments give a clear discrimination between the ranks, and the two bituminous coal appear to be identical. However, the 20 ms experiments do distinguish between these two coals, while the ranking order of the most reactive coal chars gets "mixed". Generally the new characterization method appears to be quite efficient.

The second series illustrates the only comparison with results from practice, identified so far. The three coals involved have the following conventional data:

Coal from	Ash,%	Volatiles,%	H _i kcal/kg	Softening temp.,°C
Poland	16.1	36,0	7749	1190
South Africa	12.8	28,8	7783	1340
Mozambique	17.6	36.9	7690	?

Petrographic figures show substantial differences in vitrinite and inertinite contents. The DTH/DTC/TG data seem to differ moderately and do not offer an easy interpretation. The following test results are at hand (only two coals being used in PF firing):

Coal from	Drop tube % burnt	Ignition, combustion	Not burnt in ash,%
Poland	96,1	very good	2
South Africa	87,8	rather good	6
Mozambique	94,4	-	-

The overall dkTEKNIK results grade the samples in the order: Poland, Mozambique, South Africa. The pyrolysis/reactivity results, as shown in Fig. 16 give the same order. A detailed comparison does not seem possible.

4. Summary

The results obtained do meet the prospects of a new possibility for coal characterization, in that the proposed principle seem to have a definite potential of practical interest. The method displays good reproducibility and reflects also minor differences in coal properties. The number and ranges of significant parameters appear to be limited, and standardization to optimal conditions, e.g. with regard to laser requirements, should be possible, using simplified equipment.

We have been invited by the European Common Market Authorities to examine the possible development of a commercial apparatus with the support of consultants with experience of such endeavours.

Lyngby, December 1989

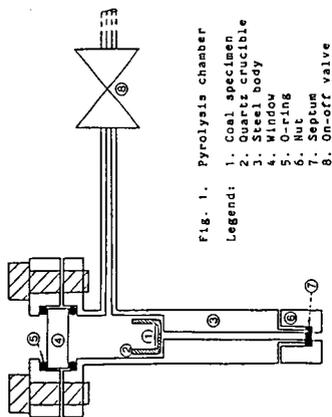


Fig. 1. Pyrolysis chamber

- Legend:
1. Coal specimen
 2. Quartz crucible
 3. Quartz body
 4. Window
 5. O-ring
 6. Nut
 7. Septum
 8. On-off valve

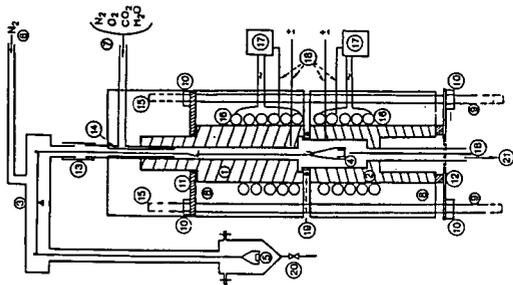
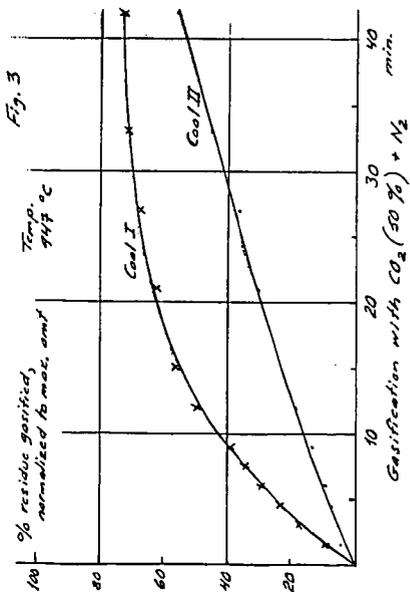
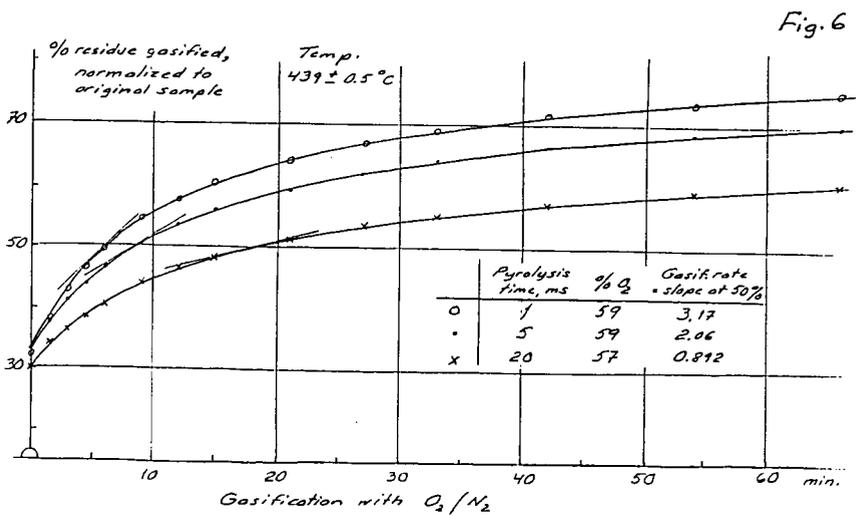
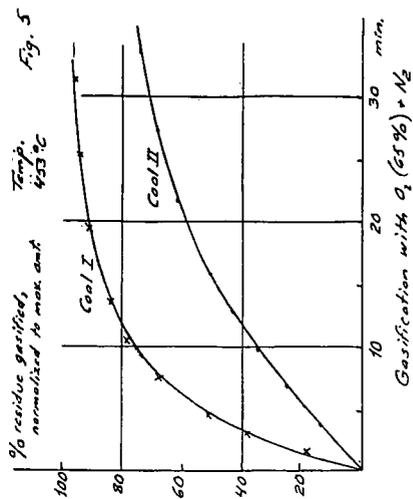
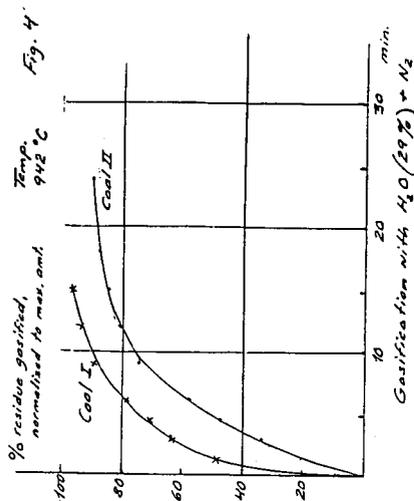


Fig. 2. Reactor furnace and microbalance

- Legend:
1. Reactor body, upper part
 2. Reactor body, lower part
 3. Micro balance
 4. Insulation
 5. Weighing pan (carrying crucible with coal specimen)
 6. Gas inlet (for protection of balance)
 7. Inlet for N_2 , O_2 , CO_2 , H_2O
 8. Insulation
 9. 4 steel bars (to keep reactor parts together)
 10. Bolting nuts
 11. Top plate
 12. Top plate (springy material)
 13. Expansion joint
 14. Mixing section
 15. Prolonged bars (acting as hanging support)
 16. Heating coil
 17. Temperature controls
 18. Thermocouples
 19. Packing
 20. Vent
 21. To cooler and chromatograph





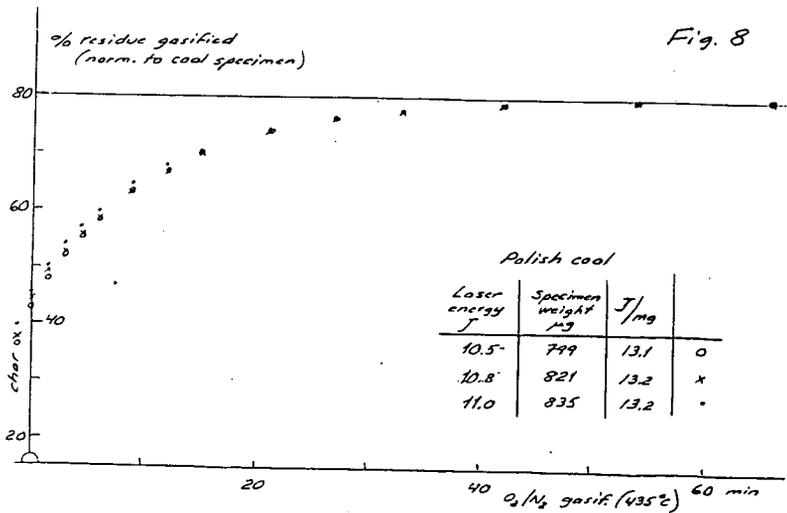
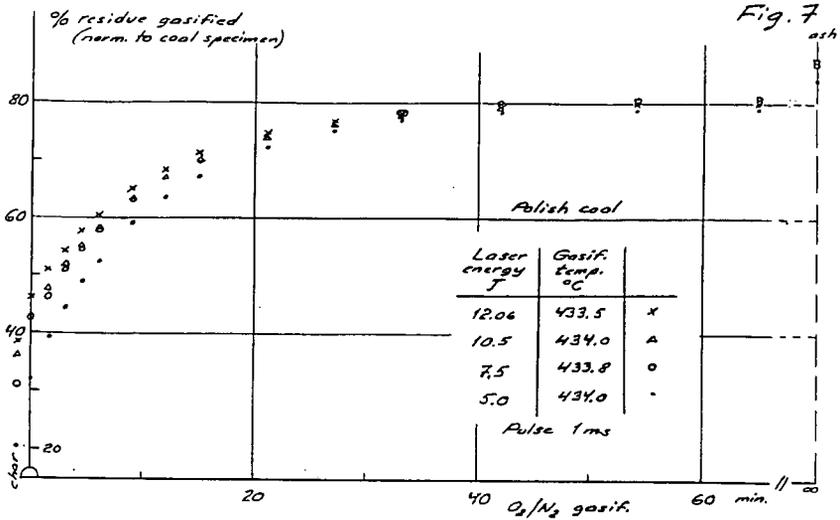


Fig. 9

