COAL AS A FEEDSTOCK FOR FULLERENE PRODUCTION AND PURIFICATION

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INTRODUCTION

Since the first availability of fullerenes in bulk,[1,2] research on these materials has fluorished rapidly. There is implication that these molecules are potentially useful[3] as lubricants, superconductors, rechargable batteries, diamond nucleators,[4] catalysts and chemical feedstocks. Fullerenes are commonly produced by the electrical arcing of graphite in helium,[1] but can also form from benzene combustion in an Ar/O_2 mixture.[5] Purification is usually performed by chromatography on silica.[6] We have recently demonstrated that fullerenes can be produced by the electrical arcing of coke derived from coking coals.[7] We have now extended the study using different Australian coals including brown coal and semi-anthracite and prepared coke from these coals by a number of different methods. Coal was also demonstrated to be a useful chromatographic material to purify C_{60}.

EXPERIMENTAL

Preparation of conductive coke rods

The primary requirement for production of fullerene from coal in this work is the preparation of conductive coke rods. Three methods of coke preparation were used.

1) laboratory coke. A finely ground coking coal was heated in an aluminium mould in an argon flow at 395°C for 24 h to form a semi-coke rod. This rod was carbonised at 1200°C in argon for 5h.

2) Coal-pitch composite. This method is suitable for both coking and non-coking coals. Finely ground coal and pitch (20 wt. %) mixtures were placed in a Swage-lok type stainless steel tube and sealed. The system was heated to 500°C for 24 h. A semi-coke rod was formed, which was carbonised at 1200°C in argon for 5 h. Additional carbonisation conditions (1200°C for 10 h, 1300°C for 1 h) was used for brown coal and neat pitch to induce electrical conductivity.

3) Oven coke. Finely ground coking coals were heated in a wall oven (0.42 m^3) under sealed condition at 1010°C for 16-19 h. Samples of coke were cut into rods for electrical arcing.

Fullerene production

Fullerene was produced by electrically arcing the coke rods in a 250 torr helium atmosphere at 23-30 V and 80-130 A a.c. or d.c. in a stainless steel chamber. The soot produced by this process was Soxhlet extracted with toluene to give crude fullerenes.

Purification of C_{60} on coal

For purification of C_{60} on coal, Yarrabee semi-anthracite (H/C 0.74, O/C 0.013) was ground and size separated. The 63-125 um size fraction was pre-washed in a Soxhlet extractor for 3 days with toluene to remove any soluble materials. A glass column was packed with this pre-washed coal (1.2 cm by 58 cm) using hexane, and crude fullerene (15 mg) was dissolved in toluene (3 ml) and loaded on the head of the column. After elution with hexane (800 ml) at a flow-rate of 2 ml/min, 8.7 mg of solid pure C_{60} was obtained from the eluate.

RESULTS AND DISCUSSION

Table 1 lists the carbon contents and ash yields for the different cokes, and fullerene yields. Infrared spectroscopy showed absorption peaks characteristic of C_{60} and C_{70} fullerenes in similar ratios (ca. 10:1 for C_{60} : C_{70}) reported for graphite as a source material[1]. The ratios have been confirmed by solid-state ^{13}C nuclear magnetic resonance spectroscopy.

All cokes tested so far produced fullerenes. Thus it appears that other conductive carbonaceous materials may also be able to produce fullerenes. An optimum fullerene yield of 8.6% was obtained from superclean Goonyella coke. This compares favourably with the yield of 9.3% obtained from graphite under identical conditions. Pitch (neat) yielded only 2% fullerenes, therefore, in the composite with coal in which pitch was present at a level 20%, the fullerenes were predominantly produced from the coal, since much higher yields were obtained from these composites. Also, the use of d.c. current rather than a.c. appears to markedly increase the yield of fullerenes from both graphite and coal.

Although coking occurs readily at 1200°C, graphitisation does not usually occur below 2500°C on these time scales[8]. The results presented here show that graphitisation is not a requirement for fullerene production by the electrical arc method.

The presence of mineral matter (ash yield) in the coal does not inhibit fullerene formation from coke, however, its presence does result in a reduced yield of fullerene. Data in Table 1 indicate that poorer fullerene yield (around 3% or less) was obtained from the oven cokes and Coalcliff composite which have over 10% mineral matter. On the other hand, Loy Yang composite, Newvale composite and superclean Goonyella coke each has under 4% mineral matter and produces 6% or more fullerene yield. The electrical resistivities of the cokes do not appear to be directly related to mineral matter contents and no clear trend can be drawn between the electrical resistivities and fullerene yield.

It appears that the method of coke preparation may also affect fullerene yield. The data are scattered, but Table 1 shows that laboratory cokes (2.3-8.6%) produce comparable fullerene yield to carbonised coal-pitch composites (2-7.7%) while oven cokes (2-3.3%) give the poorest yield.

The presence of a small amount (below 4%, Table 1) of hydrogen and heteroatoms (O, S and N) in the coke does not inhibit fullerene formation. In addition, there is no simple relationship between the coal rank and fullerene yield. Semi-anthracite (Yarrabee coal) derived composite produced 5.0% fullerene, while Loy Yang brown coal composite produced 7.7% yield, which on a coal basis is at least equivalent to, if not higher than graphite at 5.8%.

A number of reports have appeared on fullerene generation by the laser ablation of coal, graphite and mesophase in an ion cyclotron resonance (ICR) spectrometer[9-11]. These results showed that the laser power required to generate fullerenes increased from mesophase < brown coal < high rank coal < graphite. Higher laser power may be needed to break down some of the regular hexagonal structure in graphite, which then rearranges to form the five and six membered ring structure in C_{60}. On the other hand, the breakdown of the more disordered structure present in brown coal and mesophase may be accomplished with relative ease. Moreover, five and six membered rings are already present in these materials, which may assist in the formation of fullerenes. For comparison, a lower laser power requirement in the ICR experiment may relate to a higher fullerene yield in the electrical arc experiment. However, in our electrical arc experiment, a definite correlation between fullerene yield and coal rank or graphite could not be made.

CONCLUSIONS

The results presented here clearly show that a suite of coals of different ranks are capable of producing fullerenes. Moreover, for Yarrabee semi-anthracite a self-consistent process for producing fullerenes is possible. The coal can be used to produce fullerenes and also to separate pure C_{60}. The presence of mineral matter and heteroatoms does not inhibit fullerene formation but does reduce fullerene yield. The regular hexagonal carbon structure present in graphite is not a requirement for fullerene formation. In fact, a disordered carbon structure may be favourable. With the present cost of coal at $100 per tonne or less, its use as an industrial material for fullerene may greatly improve the economics of large scale production.

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Table 1. Electrical conductivities, fullerene yields, carbon contents and ash yields for coke[a] and graphite.

source carbon	electrical resistivity ohm/cm	fullerene yield (wt. %)	%C	%ash yield	%O+H+S+N[b]
I. Laboratory coke					
Goonyella[c,d]	.53	5.6	95.8	2.1	2.1
Goonyella[c,e]	.38	8.6	94.8	3.8	1.4
Goonyella[c,f]	.33	2.3	91.0	7.6	1.4
graphite[c]	.009	9.3			
graphite	.009	16.2			
II. Carbonised coal and pitch composite					
Coalcliff[c]	.07	2.0	85.2	14.5	0.3
Coalcliff	.07	3.2			
Newvale	.12	6.0	95.1	1.6	3.3
graphite[g]	.009	5.8			
Loy Yang	.38	7.7	96.5	1.8	1.7
Yarrabee	.26	5.0	95.7	4.2	0.1
pitch	.26	2.0	96.9	2.0	1.1
III. Oven coke					
Norwich Park	.10	3.3	84.2	12.1	3.7
Riverside	.09	2.5	85.4	12.0	2.6
Blackwater	.09	2.2	86.3	10.7	3.0
Goonyella	.46	2.3	85.3	11.0	3.7
Gregory	.12	2.8	85.4	11.5	3.1

a wt. % dry basis

b by difference

c electrical arcing was induced by a.c.; d.c. was used for the other experiments.

d from ultraclean coal

e from superclean coal

f from as received coal

g The fullerene generator was modified for these experiments, and the yield of fullerenes reduced significantly but consistently. Yield data for cokes below this column should be compared to this value.