CARBONIZATION OF HEXANE AND TOLUENE IN AN RF THERMAL PLASMA AT NORMAL PRESSURE

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Abstract

Carbonization of hexane and toluene has been investigated in an inductively coupled RF thermal plasma. A two level complete factorial design approach was applied to study the effect of system variables on the yield and composition of products formed. The main product of carbonization was carbon black (soot). A great number of polycyclic aromatic hydrocarbons was also identified, however, their quantity amounted a few per cent of the soot only. ESR investigations referred to the presence of insoluble hydrocarbons in the soot. There is a good reason to support that carbonization of hexane and toluene takes place according to a rather complicated mechanism in RF thermal plasma torches.

Introduction

The radiofrequency (RF) thermal plasma torches operating at atmospheric pressure produce a stable, large hot plasma region. Hence, they can favorably used to carry out high temperature chemical reactions due to the sufficient residence time of reactants in the hot region.

It is well known that carbonization of liquid precursors, such as hydrocarbons at high temperatures results in a great number of different species. Decomposition of benzene in a hot plasma zone to small fragments, like C, C_2, C_3 or C_2H was reported by Hashizume et al. [1]. Carbonization of toluene in different systems (tube furnace, electric discharges, silent electric discharges and RF thermal plasma) was investigated by us previously [2]. In the RF thermal plasma the main product was carbon black (soot), but formation of polycyclic aromatic hydrocarbons and some insoluble hydrocarbons was also detected.

On the basis of these experiences we thought appropriate to investigate the carbonization of toluene and hexane in an RF thermal plasma torch in a systematic way. The experiments were aimed at learning the effect a reaction conditions on the

yield and composition of products formed. Furthermore, we wanted to compare the decomposition and recombination behavior of hexane and toluene on the given conditions.

Experimental

The RF induction plasma torch employed by us was of a standard design with a quartz glass plasma confident tube (27 mm I.D.). The tube was connected to air-cooled quenching and powder collection sections. The plasma power was provided by a 3-turn induction coil from an RF generator operating at an oscillator frequency of 27.17 MHz.

High-purity argon was used as plasma and sheath gases and also as the carrier gas of reactants. Analytical grade hexane or toluene were injected in a swirl direction, through a transverse slot into the plasma tail, downstream of the coil. The distance between the bottom of the coil and the slot was 10 and 20 mm, respectively. Below the injection region, where the gas phase was cooling gradually along the stream, solid soot appeared. The soot was mainly collected on the wall of the confident tube. Only a minor portion of the soot were captured in the powder collection section.

Flow rates of plasma gas (7 $l \cdot min^{-1}$ (STP)) and sheath gas (19 $l \cdot min^{-1}$ (STP)) were adjusted on the basis of our previous experiments.

System variables, effect of which we wanted to study included plate power, quality and feed rates of reactants and the height of injection into the plasma tail. Each variable was set at two levels (Table 1) and a complete factorial design approach was applied for the experimental design. In order to have enough product for the analysis, duration of runs was at least 20 minutes in all cases.

Table 1 System variables and their levels

System variables	Levels		Type of variable
	Lover	Upper	
Plate power (P, kW)	2.1	2.9	quantitative
Feed rates of reactants (R, $g \cdot min^{-1}$)	0.3	0.6	quantitative
Height of injection (L, mm)	10	20	qualitative
Chemical nature of precursor	Toluene(T)	Hexane(H)	qualitative

The soot collected from the reactor wall and the powder collection section was extracted by toluene using the Soxhlet method. Both the soot, the extract and the solid residue of extraction were studied by ESR. The extracts were subjected to GC-

MS and HPLC analysis, too. SEM micrographs were prepared to study the morphological features of powders. No quantitative experiment was made so far to analyze the volatile products of carbonization.

Results and discussion

Conditions and results of the two levels complete factorial design experiments are summarized in Table 2. The soot yield (Y_S) is an overall indicator of the system performance in terms of soot formation and collection, because the very fine soot leaving the experimental system with the exhaust gas was disregarded in the calculation of Y_S. The amount of exhausted soot is estimated to be 5-10% of the powder formed. Quantity of the extractable compounds reached only a few per cent of the soot mass, as it was indicated by the E/S values in Table 2.

Table 2 Conditions and results of factorial design experiments

No	P (kW)	Pre-cursor	R ($g \cdot min^{-1}$)	L (mm)	m* ($kWh \cdot kg^{-1}$)	Y_S (%)	E/S (%)
1	2.1	H	0.670	10	0.028	4.2	7.9
2	2.9	H	0.637	10	0.216	33.9	1.8
3	2.1	H	0.240	10	0.016	6.7	6.7
4	2.9	H	0.255	10	0.068	26.7	1.7
5	2.1	H	0.622	20	0.069	11.1	4.3
6	2.9	H	0.632	20	0.211	33.4	2.5
7	2.1	H	0.285	20	0.031	10.9	1.7
8	2.9	H	0.249	20	0.076	30.5	1.8
9	2.1	T	0.590	10	0.190	32.2	0.3
10	2.9	T	0.535	10	0.244	45.6	1.0
11	2.1	T	0.350	10	0.090	25.7	0.7
12	2.9	T	0.254	10	0.118	46.5	3.6
13	2.1	T	0.613	20	0.198	32.3	3.2
14	2.9	T	0.640	20	0.328	51.2	1.5
15	2.1	T	0.325	20	0.092	25.9	7.1
16	2.9	T	0.305	20	0.159	52.2	1.0

m* formation rate of the soot, Y_S soot yield, E/S extract/soot ratio

The main product of carbonization is a very fine soot consisting of uniform spherical particles (Fig. 1). Specific surface area of the powder from Run No. 11 is 160 $m^2 \cdot g^{-1}$, and its mean particle size is equal to 25 nm.

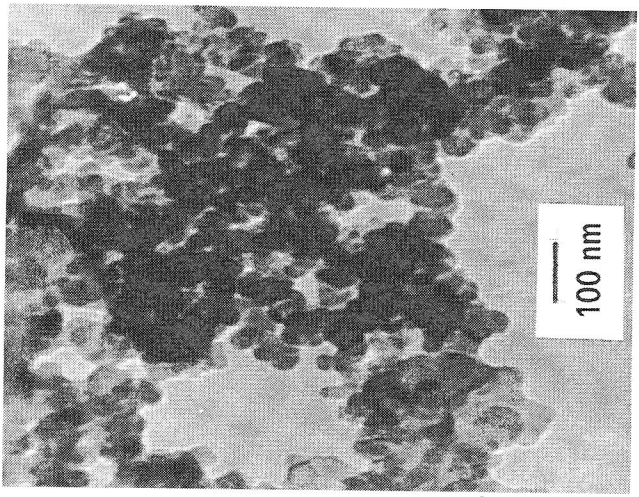

Fig. 1 SEM micrograph of the soot produced in Run No. 11.

Plotting of the Y_S and E/S values (Fig. 2) for the experiments in which toluene was subjected to carbonization revealed that

(i) at the higher plate power higher yields were achieved than at the lower ones;

(ii) injection of the toluene at a distance of 20 mm from the coil resulted in a bit higher yields as compared to injections at a distance of 10 mm, i.e. injection into a tail flame region of lower temperature was more favourable in terms of soot yield;

(iii) there was no definitive tendency as far as the effect of decreased feed rate on the yield is concerned;

(iv) the soot yield and the amount of extract changed in opposite directions: higher yields were accompanied with lower E/S ratio.

Similar phenomena were observed in the case of hexane, as well. However, smaller yields and in most cases higher extract ratios was detected in these experiments than in the corresponding tests with toluene.

It can be concluded from these results that both the soot and the extract yields are predominantly affected by the temperature and fluid dynamics of the plasma. Concentration of reactants in the gas stream is of less importance.

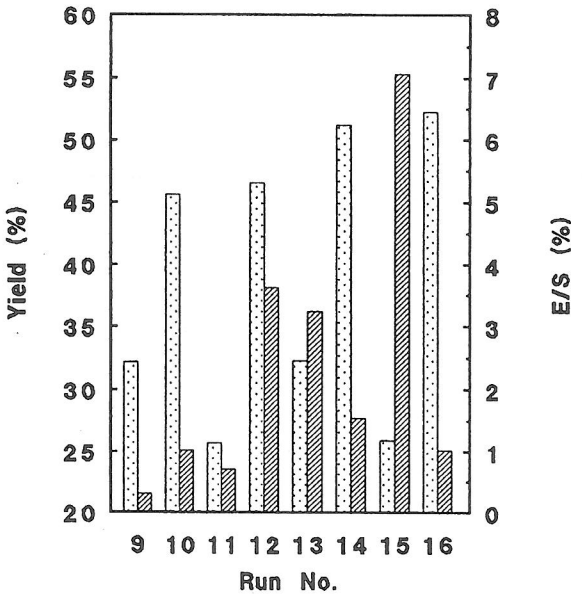

Fig. 2 The soot and extract yields in the case of toluene carbonization

The GC-MS analysis of the extract from Run No. 11 showed the presence of polycyclic aromatic hydrocarbons (Table 3).

Table 3. Compounds identified by the GC-MS analysis of the extract of Run No 11.

1H-indene	Pyracyclene	1-Methylpyrene
Azulene	1,2-Diphenylmethane	Benzo(g,h,i)fluoranthene
Naphthalene	4,4'-Dimethyl-1,1'-Biphenyl	Chrysene
1-Methylnaphthalene	Anthracene	Naphthacene
2-Methylnaphthalene	Phenanthrene	1-Methylchrysene
Acenaphthylene	9,10-Dihydroanthracene	4,5-Methanochrysene
Biphenyl	1-(p-Tolyl)-2-phenyl-ethane	9-Phenylfluorene
1,1'-Biphenylene	1-Phenylnaphthalene	Benzo(k)fluoranthene
3-Methylbiphenyl	Acephenanthrylene	Benzo(a)pyrene
4-Methylbiphenyl	2-Phenylnaphtalene	Benzo(e)pyrene
9H-Fluorene	4,5-Dihydropyrene	Perylene
Diphenylmethane	Fluoranthene	Benzo(g,h,i)perylene
1H-Phenalene	Pyrene	

From the regularities of the relative heights of the peaks in the mass spectrum an interesting rule could be concluded: the molecular weight was increasing by 24 or 26 in each step, i.e. either an acetylide group or an acetylene molecule joined to the different ring systems.

On the basis of previous experiments, formation of hydrocarbons of high molecular weight was probable, as well. However, no hydrocarbon species of high molecular weight could be detected in the extract obtained from Run No. 11. It must be bourn in mind that the situation is rather special in the case of RF thermal plasma reactors. The volatile products leave the system, while the less volatile products are adsorbed on the soot. Hence, lack of hydrocarbons of high molecular weight in the extract does not necessarily mean that they were not formed in the given case. An obvious possibility is that these species are so strongly adsorbed that they can not be extracted. Some further reactions of the particular hydrocarbons may also take place on the surface of carbon formed. Some observations support this possibility.

The soot was also analyzed for insoluble hydrocarbons. These species exhibit a strong ESR signal. The ESR spectrum of the soot from Run No. 11 referred to the presence of free radicals of at most two types. The concentration ratio of these two sets of radicals was 10:1. The soot was then extracted by toluene. There was no decrease in the concentration of radicals in the solid phase, and we could not detect any ESR signal in the extract. However, the ESR signals in the extracted soot became narrower by a factor of three. Thus the interaction of radicals became more intensive, probably due to the decrease of the relative distance between the centres.

No direct evidence was furnished on the formation of fullerenes in the experiments in question. However, according to preliminary HPLC measurements, there was a very broad band between the expected C_{60} and C_{70} peaks in the products from Runs 2, 4 and 8 (Table 2). Further detailed investigations are required to elucidate the chemical nature of the corresponding constituents.

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