Optimization of Benzene Synthesis for Radiocarbon Dating by Response Surface Method

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Response surface method was applied to the predicting optimum conditions of benzene synthesis for radiocarbon dating. The weight of carbon dioxide, the temperature of lithium container for producing acetylene and the activation temperature of catalyst which was used for the cyclization of acetylene to benzene were used as experimental factors. The yields of benzene synthesis were measured from twelve experiments which were carried out under various experimental conditions. The polynomial equation was obtained by using three experimental factors and yields. The validity of polynomial equation was confirmed by comparing the calculated yields with the experimental ones.

Introduction

The benzene synthesis from carbon or carbon dioxide is of interest because of the determination of radiocarbon dating. The process of the benzene synthesis includes conversions of carbon dioxide to acetylene and of acetylene to benzene. Especially, in the various methods of acetylene synthesis,[1,2] the method reported by Barker[2,3] has been frequently adopted for the conversions of carbon dioxide to acetylene.

Firstly, carbon dioxide was converted lithium carbide by reaction with a molten lithium metal. The preparation of lithium carbide has been proceeded in the temperature of ranges from 650 °C to 800 °C according to the previous other studies.[2-5] The lithium carbide was cooled and then converted to acetylene by a hydrolysis.[5-7] Secondly, the conversion of acetylene to benzene has been also interested in the catalyst and the activation temperature of catalyst. Diborane[7] and a transition metal ion activated silica-alumina catalysts[5,6,8] have been used as the activation catalyst. In recent years, the catalyst activated by chromium and vanadium has been often used. The yield of conversion reaction from acetylene to benzene is controlled by the activation temperature of catalyst. Consequently, the benzene synthesis is controlled by the quantity of carbon dioxide, the temperature of lithium container for producing acetylene, and the activation temperature of catalyst which is used for the cyclization of acetylene to benzene. Therefore the optimum condition of benzene synthesis is extremely complex.
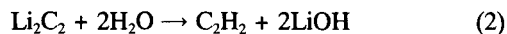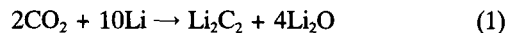
The most common approaches for optimum conditions of benzene synthesis are usually based on an univariate sequential optimization. However, such univariate sequential optimization would not be effective in locating the true optimization in some cases. Therefore, multivariate simultaneous optimization such as a response surfaces is preferable.[9] The multivariate approach such as factor analysis has been investigated in the interpretation of the overlapped X-ray fluorescence spectra[10] and X-ray diffraction patterns.[11]

And the multivariate simultaneous optimization has been applied to optimization of supercritical fluid extractions[12] and supercritical fluid chromatography.[13]

In this study, the systematic multivariate optimization was applied to the optimization of benzene synthesis for the radiocarbon dating. The weight of carbon dioxide, the reaction temperature of lithium container for producing acetylene and the activation temperature of catalyst were used as experimental factors for optimization. The polynomial equation for the optimum synthesis of benzene was obtained from the experimental factors and synthetic yields of benzene. The validity of polynomial equation was confirmed by comparing the experimental and calculated yields.
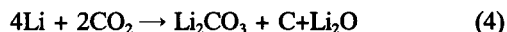
Experimental

An installation for the benzene synthesis was supplied by TASK (Technical and Applied Scientific Knowledge). The synthesis of benzene was proceeded on the vacuum system and carried out by the following reactions,[3,5]

$$2CO_2 + 10Li \rightarrow Li_2C_2 + 4Li_2O \tag{1}$$

$$Li_2C_2 + 2H_2O \rightarrow C_2H_2 + 2LiOH \tag{2}$$

$$3C_2H_2 \rightarrow C_6H_6 \tag{3}$$

The carbon dioxide could be originated from the oxidizing or burning of carbon containing samples. The carbon dioxide was converted to lithium carbide by reaction with lithium metal in the absence of air. The weight of carbon dioxide used was represented as the weight of carbon. The weights of carbon dioxide used in experiments were 2 g, 3 g, 4 g, 4.8 g, 4.96 g and 5.6 g as the weights of carbon, respectively. The commercial carbon dioxide with a purity of 99.99% was used and lithium metal bar was supplied by Strem Chemicals (USA).

The reaction (1) was proceeded at various temperatures of 700, 730, 760 and 790 °C. The yield of reaction (1) could be reduced by the following secondary reactions,[14,15]

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$$4Li + 2CO_2 \rightarrow Li_2CO_3 + C + Li_2O \qquad (4)$$

$$Li_2O + CO_2 \rightarrow Li_2CO_3 \qquad (5)$$

These losses can be diminished by heating the reaction mixture to 900 °C as according to Tamers.[8] The lithium carbonate decomposes to a significant extent above 600 °C, which reverses reaction (5). At the temperature of 900 °C, the carbon dioxide regenerated is converted to the lithium carbide by the reaction (1). The free carbon of reaction (4) is converted by the following reaction (6),

$$2C + 2Li \rightarrow Li_2C_2 \qquad (6)$$

The hydrolysis of the lithium carbide which was cooled to room temperature, was proceeded with a quantitative yield as shown in reaction (2). During the hydrolysis of the lithium carbide, a hydrogen gas could be evolved by the decomposition of lithium hydride, which was formed by the reaction of the remaining lithium and water. The evolving acetylene, hydrogen and remaining moisture were dried over a dry ice-alcohol trap and then passed over the column impregnated with phosphorous oxide and ascarite before the acetylene was frozen out by the liquid nitrogen.

The acetylene was trimerized to benzene below 200 °C to reduce a secondary reaction as according to the result reported by Tamers[8] and Belluomini et al.[5] The chromium activated silica-alumina catalyst was used for the cyclization of acetylene to benzene. The catalyst used was activated at various temperatures of 350, 400, 450, 500, 600 and 700 °C, respectively, during 2 days. The benzene synthesized was collected in a vial of known weight and the yield of benzene was determined by weighing.

The purity of benzene was checked by using a gas chromatograph (HP 5890) linked to a mass spectrometer detector (HP 5988A). The capillary column (SE54) with a length of 25 m and an inner diameter of 0.2 mm and He gas as a carrier gas were used.

Results and Discussion

Twelve experimental conditions selected for the benzene synthesis are listed in Table 1. The weight of carbon dioxide used to produce acetylene was ranged from 2.0 g to 5.6 g as the weights of carbon. The temperature of lithium container for producing acetylene was ranged from 700 °C to 790 °C. And the activation temperature for catalyst which was used for trimerization of acetylene to benzene was ranged from 350 °C to 700 °C. The experimental conditions were normalized as the range between low value (0%) and high value (100%). The yields of benzene synthesis obtained from twelve experiments are also listed in Table 1.

The yield of benzene synthesis is represented by three experimental factors as the following polynomial equation,

$$Y(\%) = b_0 + \sum b_i \, x_1^l \, x_2^m \, x_3^n \qquad (7)$$

where, Y is the predicted yield(%) of benzene synthesis. The b_0 and b_i are coefficients of polynomial equation and x_1, x_2 and x_3 represent the normalized values of the experimental factors described above, *i.e.*, the weight of carbon, the temperature of lithium container for producing acetylene and the activation temperature for catalyst, respec-

Table 1. Experimental factors for benzene synthesis and yields

Experiment no.	Weight of carbon (g)	Temperature[a] (°C)	Temperature[b] (°C)	Benzene yield (%)
1	2.00	730	450	84.8
2	4.96	700	350	81.2
3	4.96	730	400	87.4
4	3.00	730	450	89.6
5	4.00	730	450	85.1
6	4.96	760	600	91.1
7	4.80	730	450	90.9
8	5.60	730	450	97.1
9	4.96	790	700	89.5
10	4.96	760	450	86.8
11	4.96	790	450	80.8
12	4.96	730	450	88.3

[a] The temperature of lithium container for producing acetylene.
[b] The activation temperature of catalyst used for the cyclization of acetylene to benzene.

tively. The *l*, *m* and *n* are orders of polynomial equation. The coefficients of polynomial were obtained using Basic program on the basis of Ref. 9.

The polynomial equation obtained from three experimental factors and synthetic yield of twelve experiments listed in Table 1 is as follows,

$$Y(\%) = 0.770 + 0.348x_1 + 0.316x_2 + 0.094x_3 + 0.026x_2x_3$$
$$- 0.986x_1^2 - 0.566x_2^2 + 0.762x_1^3 + 0.211x_2^3 \qquad (8)$$

where, x_1, x_2 and x_3 are the normalized values of the three experimental factors. The coefficients for the terms of x_1x_2, x_1x_3, x_3^2 and x_3^3 are negligibly small and not represented in polynomial equation. From the comparing of the coefficients of polynomial equation, the weight of carbon (x_1) and the temperature of lithium container for producing acetylene (x_2) had larger effect than the activation temperature for catalyst (x_3). Since the multiple correlation coefficient R^2 was moderately high as 0.98 (1.0 is the best possible), the polynomial equation of the optimum condition
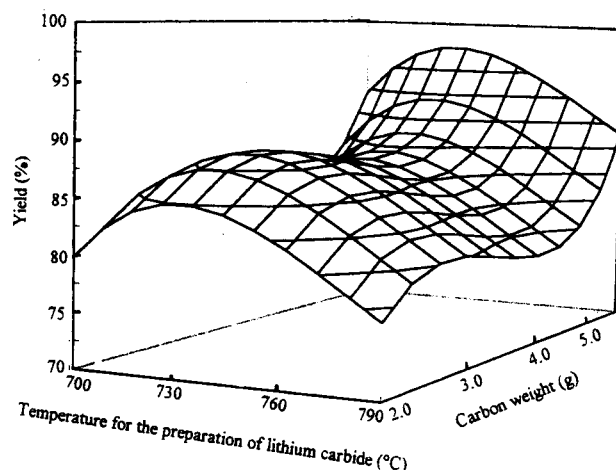
Figure 1. Contour map showing the yield of benzene synthesis when the activation temperature of catalyst is 450 °C.
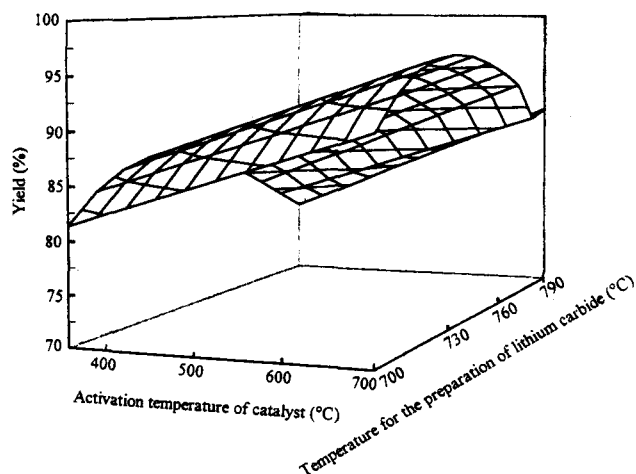
Figure 2. Contour map showing the yield of benzene synthesis at carbon weight of 4.96 g.

Table 2. Comparison of experimental (Y_{exp}) and calculated (Y_{cal}) yields

Experiment no.	Weight of carbon (g)	Temperature[a] (°C)	Temperature[b] (°C)	Y_{exp} (%)	Y_{cal} (%)
a	4.96	730	450	90.3	89.2
b	4.96	760	500	89.5	88.2
c	4.96	700	450	84.6	84.0

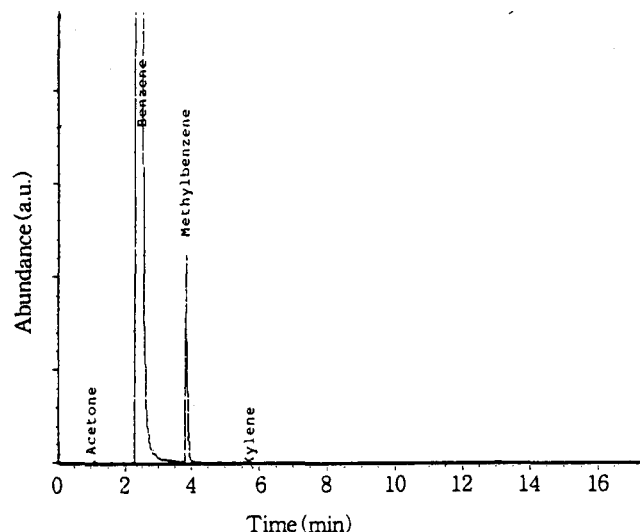[a] the temperature of lithium container for producing acetylene.
[b] the activation temperature of catalyst used for the cyclization of acetylene to benzene.

for benzene synthesis is considerd to be accurate representations of the measured values.

The contour map for the yield of benzene synthesis at x_3 of 0.29 (the activation temperature of catalyst is 450 °C) is shown in Figure 1. When the carbon weight is above 4.8 g and the temperature of lithium container for producing acetylene is about 730 °C, the yield of benzene synthesis is above 90%.

Figure 2 shows the contour map which indicates the yield of benzene synthesis at x_1 of 0.82; that is, the weight of carbon equal to 4.96 g. The result indicates that the yield above 90% for benzene synthesis is obtained when the temperature of lithium container for producing acetylene is 730 °C and the activation temperature of catalyst is above 450 °C. The benzene yields above 80% were obtained from the twelve experiments listed in Table 1 and from the results shown in Figure 2. Polach[16] and Panarello et al.[17] reported that the isotopic fractionation was minimal when the conversion yield of carbon dioxide to benzene was higher than 80%. Therefore, the isotopic fractionation was negligible in this work.

To confirm the validity of the polynomial equation (8), three experiments were selected and then the yields were calculated by using the polynomial equation (8). The results of the experimental conditions, experimental yields and calculated yields are listed in Table 2. The results obtained between the experimental and calculated yields are reasonably good agreement within 1.5%. This result indicates

Figure 3. Total ion chromatogram of benzene synthesized from the shell sample under condition of point *a* represented in Table 2.

that the polynomial equation obtained can serve to optimize experimental conditions for benzene synthesis.

The purity of benzene synthesized from the shell sample excavated from Anmyun-do, Chungnam was analyzed by GC/MS. The benzene synthesis was carried out at the same condition as point *a* represented in Table 2, that is, x_1 (the carbon weight) of 4.96 g, x_2 (the temperature of lithium container for producing acetylene) of 730 °C and x_3 (the activation temperature of catalyst) of 450 °C, respectively. Figure 3 shows the total ion chromatogram of benzene synthesized. The purity of benzene having the yield above 89% was measured to 98.8%. And methylbenzene, xylene and acetone were detected as impurities below 1.2%.

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Attenuation of Background Molecular Ions and Determination of Isotope Ratios by Inductively Coupled Plasma Mass Spectrometry at Cool Plasma Condition

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Isotope ratios of K, Ca, Cr and Fe are measured at cool plasma condition generated using high carrier flow rate and relatively low RF power of 900 W. Background molecular ions are suppressed to below 100 counts which give isobaric interference to the analytes. The background ions show different attenuation characteristics at increased carrier flow rate and hence for each element different carrier flow rate should be used to measure isotope ratios without isobaric interference. Isotope ratios are measured at both scan and peak-hopping modes and compared with certified or accepted ratios. The measured isotope ratios show some mass discrimination against low mass due to low ion energy induced from a copper shield to eliminate capacitive coupling of plasma with load coil.

Introduction

Thermal ionization mass spectrometry (TIMS) has been used extensively in the geological, nuclear, and analytical sciences for isotope ratio measurements. In 1982 a new technique, inductively coupled plasma mass spectrometry (ICP-MS), was introduced to analysts. ICP-MS is now taking the place of TIMS in many fields of isotope ratio measurements. ICP-MS offers a number of advantages over TIMS in spite of relatively poor precision (about 0.2%) of isotope ratio measurements.[1] Most importantly, sample throughput is rapid. ICP-MS requires typically 1-5 min measurement time and involves less sample pretreatment, while TIMS requires long measurement time of about 1 hour per sample and prolonged sample pretreatment. Thus ICP-MS is an important analytical tool for isotope ratio measurement when many samples have to be analyzed rapidly.

For almost six years after introduction of the first commercial ICP-MS, measurements of isotope ratios of K, Ca, Cr, and Fe had been considered impossible because of huge background peaks in the mass range 39-57.[2,3] Various methods have been attempted to attenuate background peaks giving isobaric interference to the elements. An electrothermal vaporizer (ETV) was used as an alternative sample introduction device to reduce especially ^{40}ArO peak for determination of Fe.[4-7] With the ETV, solvent was completely eliminated during drying step and dry salts were subsequently vaporized into the plasma so that ^{40}ArO intensity could be reduced to around 1000 counts per second (cps). It was, however, difficult to measure isotope ratios with precision better than 1%, because the ETV, in principle, generated transient signals lasting only 2-3 seconds. Furth-

ermore, it was not easy to get accurate isotope ratios due to the presence of background intensity around 1000 cps. Addition of foreign gases such as N_2, H_2, CH_4 and Xe to the plasma or carrier argon line was also attempted to suppress the ^{40}ArO background peak.[8-10] These foreign gases are known to scavenge oxygen in the plasma by gas-phase collisions. It was also not easy to implement this technique because the plasma became unstable when the foreign gases were introduced into the plasma.

In 1986, Gray published his work on reduction of plasma potential with various load coil geometries.[11] He used a screen shield to cut off capacitive coupling between the load coil and plasma, and thereby to reduce plasma potential. He also reported that plasma generated with the screen shield gave unfavorably higher oxide ratios than that with normal load coil. In 1988, Jiang et al. reported that K isotope ratios could be measured with ICP-MS at cool plasma condition generated using low forward power and high carrier flow rate.[12] At the cool plasma condition, they could reduce ^{38}ArH and ^{40}ArH background peaks to below 100 cps. They added a special note that their Elan 250 ICP-MS with center-tapped load coil generated little or no electrical discharge at the interface so that ^{38}ArH and ^{40}ArH background peaks could be suppressed, and that the same result could not be obtained with other ICP-MS instruments with normal load coil due to the electrical discharge at the interface.

Based on the ideas of Gray's shield coil to reduce electrical discharge and Jiang's cool plasma to suppress argon molecular ions, new commercial ICP-MS instruments were introduced which could determine low ppt levels of K, Ca, Cr, and Fe by attenuation of fundamental background ions.