The continuity of the net thermal current from the interior to the exterior gives

$$Q_{\mathrm{RG-,C}} + Q_{\mathrm{RG-,R}} + Q_{\mathrm{RA,R}} = Q_{\mathrm{RA,R}} + Q_{\mathrm{G-G+,C}} = Q_{\mathrm{RA,R}} + Q_{\mathrm{G+A,R}} + Q_{\mathrm{G+A,C}} \quad (7)$$

Equation 7 represents two simultaneous equations with two unknowns, $T_{\mathrm{G-}}$ and $T_{\mathrm{G+}}$, which can be solved readily by iterative numerical techniques. In Eq. 7 we have added the $Q_{\mathrm{RA,R}}$ contribution to all terms to illustrate continuity of the net energy transport. This term cancels out in the determination of the glass temperatures. In the text we specifically considered the two limiting cases of IR opacity (glass) and IR transparency (rock salt or polyethylene). Using the techniques sketched here, any results between these limits can be obtained readily. For the case of glass, which is opaque to room temperature thermal IR, $\epsilon_{\mathrm{G-}} = \epsilon_{\mathrm{G+}} = 0.88$. For the cases of IR-transparent materials, $\epsilon_{\mathrm{G-}} = \epsilon_{\mathrm{G+}} = 0$, while the IR transmittance is reduced from unity only by the dual-surface IR reflectivity. The single-surface thermal IR reflectance of glass is $\simeq 0.12$. Assuming that the IR-transparent medium has the same single-surface reflectivity for a lambertian (diffuse) IR source as glass, the dual-surface transmittance is given in terms of the single-surface reflectivity r by the relation

$$\tau = (1-r)^2/(1-r^2) \cong 0.79 \quad (8)$$

S. D. Silverstein
Corporate Research and Development,
General Electric Company,
Schenectady, New York 12301

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Total Synthesis Benzene and Its Derivatives as Major Gasoline Extenders

Abstract. *Synthesized benzene and simple alkylated derivatives are proposed as nonpetrochemical gasoline components. Feasible raw materials include coal, coke, charcoal, and carbonaceous wastes. The basic synthesis consists of the formation of lithium carbide by reaction of the metal with carbon, hydrolysis of the carbide to acetylene, cyclization of acetylene to benzene, and regeneration of lithium metal. Total synthesis benzene is substantially different from other synthetic hydrocarbon fuels in that its hydrogen content is obtained from water so that hydrogen gas is not needed as a major reactant.*

Total synthesis benzene (TSB) should be considered as a possible fuel for internal combustion engines. This proposal is an alternative to those approaches to coal liquefaction that involve deep or extensive hydrogenation, pyrolysis, and the generation of alcohols. These synthetic hydrocarbon methods depend upon hydrogen gas as a major reactant, whereas in the TSB method the hydrogen is obtained from a water reaction.

Benzene synthesis is the basis of a standard technique now employed in radiocarbon dating (*1–3*). A large variety of starting materials can be used, including charcoal, other chars, organic substances, carbonates, and carbon dioxide. Because of the limited size of these samples, extensive efforts have been made over the past years to optimize the synthesis efficiency, reliability, and ease of operation. At the present time, 90+ percent yields are routinely obtained (*4, 5*).

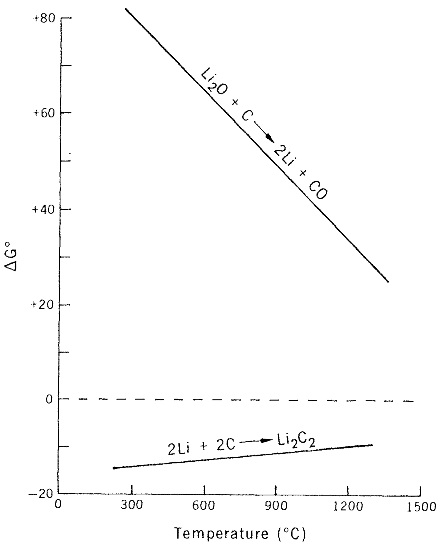

Fig. 1. Standard Gibbs free energies for the formation of lithium carbide and for the reduction of lithium oxide with carbon.

To produce TSB in industrial quantities, a modified synthesis with recycled lithium is outlined in Table 1. The fused salt electrolyses of both alkali metal hydroxides (procedure 1) and chlorides (procedure 2) are established industrial procedures (*6*). The chloride procedure has the advantage of greater electrolysis efficiency and the production of a valuable by-product, chlorine gas. The hydroxide electrolysis route is simpler but consumes more electricity because of a side reaction of water with the metal. The alternative technique in which lithium oxide is reduced with carbon (procedure 3) can be carried out with most of the energy supplied by direct combustion. These methods regenerate the metal intermediate used in the production of acetylene.

Standard Gibbs free energy changes (ΔG°) for the formation of lithium carbide and for the reduction of lithium oxide with carbon are shown in Fig. 1. In the latter reaction, the carbon monoxide generated is expeditiously removed with a good vacuum system; lithium vapor is also produced. Extraction of these two gaseous products from the immediate reaction zone displaces the equilibrium and results in usable oxide reductions, despite the positive ΔG° values. Lithium vapor is condensed in the presence of feedstock carbon to form the carbide.

The introduction of pure carbon into the reactor by the decomposition of carbon monoxide feedstock is also a possible approach. This procedure eliminates the ash separation step. Carbon monoxide is continuously produced when carbon dioxide is passed over a heated char. An alternative would be to

Table 1. Reactions for the total synthesis of benzene with lithium intermediate recycling.

Reaction	Temperature (°C)	Remarks
$2\,Li + 2C \rightarrow Li_2C_2$	950	Exothermic
$Li_2C_2 + 2H_2O \rightarrow C_2H_2 + 2LiOH$	100 to 400	Exothermic
Feedstock ash removed	100 to 400	Filtered, wash water used in carbide hydrolysis step
Procedure 1		
LiOH dried	400	Endothermic, under vacuum
$4LiOH \rightarrow 4Li + O_2 + 2H_2O$	400	Endothermic, fused salt electrolysis, O_2 collected
Procedure 2		
$LiOH + HCl \rightarrow LiCl + H_2O$	400	Exothermic
LiCl dried	400	Endothermic, under vacuum
$2LiCl \rightarrow 2Li + Cl_2$	400	Endothermic, fused salt electrolysis, Cl_2 collected
Procedure 3		
$2LiOH \rightarrow Li_2O + H_2O$	800 to 1000	Endothermic, under vacuum
$Li_2O + C \rightarrow 2Li + CO$	1000 to 1300	Endothermic, under vacuum, CO collected, Li vapor condensed
Final step		
$2C_2H_2 \rightarrow C_6H_6$	100 to 600	Exothermic, lower temperature with catalyst or higher-temperature pyrolysis

use the gas generated in underground mine fires. When oxygen is fed into such fires, the proportion of carbon monoxide in the gas mixture increases. Sulfur in the coal remains largely underground with the ash (*7*).

Cyclization of acetylene to benzene for radiocarbon dating was first carried out by noncatalytic pyrolysis (*1*). The use of Reppe (*8*), Zeigler (*9*), and diborane-activated catalysts (*2*) followed. More recently, vanadium- and chromium-activated silica-alumina pellets, operating at about 100°C, were found to be applicable (*3*). These slowly deactivated catalysts are conveniently reactivated by heating in the air (*4*). However, the noncatalytic conversion of acetylene to benzene by pyrolysis is now being reconsidered, since the higher temperatures involved (up to 600°C) permit waste heat from that reaction to be efficiently exploited. A combustion enthalpy loss of 16 percent results from the cyclization of acetylene to benzene.

Synthetic benzene produced by this system could be used not only as a gasoline extender but also in industrial applications. The industrial uses of the intermediate actylene should also be considered.

The following advantages can be stated for TSB production:

1) It can be derived from a large variety of nonhydrocarbon feedstocks. The synthesis is efficient and requires no hydrogen gas, no pressurized systems, and no final refinery (cracking and reforming) operations.

2) Although benzene produced from calcium carbide is presently more expensive than benzene produced from petroleum (about \$0.37 versus \$0.22 per liter) (*10*), it is expected that the recyclable lithium carbide synthesis could substantially decrease the costs of the carbide procedure. The price of TBS obtained by this method would approach that of benzene obtained from the petrochemical route.

3) Benzene can be readily alkylated to form other simple aromatics. Benzene and its derivatives constitute 30 to 50 percent of unleaded gasoline (*11*).

4) The octane number (RON) of benzene is 108, and that of its simple derivatives is between 104 and 106. The volumetric heat of combustion of benzene is 20 percent greater than that of most gasolines.

5) Benzene and its simple derivatives mix in all proportions with ordinary gasoline. They have suitable volatility for use in present gas engines, do not significantly absorb water, and are not subject to phase separation.

6) There is no sulfur in TSB, even when it is synthesized from materials of high sulfur content; TSB also contains no nitrogen or organometallic components. Feedstock ash separation is efficient and facile.

7) The use of TSB and its derivatives could provide major fuel components for internal combustion engines independent of the need for petroleum starting materials.

However, two important disadvantages for TSB and its derivatives must be considered:

1) New engineering techniques would have to be developed for a TSB industry.

2) Benzene is more toxic than the average gasoline component. Fuel containing substantial quantities of the liquid would need to be handled with reasonable precaution (*12*). The benzene derivatives are less toxic than benzene itself.

A number of metals have been examined for use as recyclable carbides. Lithium is favored for several reasons. Because of its very low atomic weight, considerably less lithium needs to be manipulated than would be the case with other metals. It readily forms high yields of the carbide; the single oxidation state reduces the possibility of side reactions. Lithium metal and lithium carbide react less vigorously with water than other alkali metals or alkaline-earth metal carbides. The hydroxide and carbonate can be decomposed to the oxide at reasonable temperatures, in contrast to the corresponding compounds of other alkali metals. In addition, the water solubility characteristics of lithium compounds facilitate feedstock ash separation. The ash can also be filtered from molten lithium hydroxide at temperatures used in the electrolysis reaction. Lithium mineral resources are large, especially when both pegmatites and brines are considered (*13*).

The recyclable carbide route to acetylene, benzene, and their derivatives should be examined in light of uncertainties in the present petroleum supply and the possibility of future world shortages. Although the total synthesis hydrocarbons are not, at present, commercially competitive with petrochemicals, it is essential to begin to consider alternatives that could slow the rate of depletion of petroleum reserves and reduce dependency on this fossil material. In any case, as various national liquid and gaseous hydrocarbon deposits become exhausted, the real cost of imported petroleum will eventually exceed that of totally synthetic compounds for most nations.

M. A. TAMERS
Nova University, Life Sciences Center,
Fort Lauderdale, Florida 33314

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9 February 1976

Radioimmunoassay for Colchicine in Plasma and Urine

Abstract. *A radioimmunoassay for the measurement of colchicine (in quantities as small as 0.05 nanogram) in plasma and urine was developed with the use of an antibody from immunized rabbits. After the intravenous injection of 2 milligrams of colchicine in seven subjects, the calculated zero-time concentration in the plasma was 2.9 ± 1.5 micrograms per deciliter, and the mean half-time in the plasma was 58 ± 20 minutes. Declining, but measurable, amounts of colchicine could be detected in urine up to day 9 after the drug was administered.*

Colchicine has been used in the therapy of the acute gouty attack for more than 150 years. It remains a drug of choice for control of the acute gouty attack (*1*) and is widely used as prophylactic therapy. If treatment begins within a few hours after the onset of the attack, more than 90 percent of patients respond within 12 to 48 hours (*2*). Colchicine given in small daily doses abolishes recurrences completely or reduces the frequency of attacks in 93 percent of patients with gout (*3*). However, the toxicity of this drug and methodologic problems resulted in little, or no, knowledge of pharmacokinetics of this agent. Plasma and urinary colchicine levels based on an isotopic dilution technique have been reported (*4*). ^{14}C-labeled colchicine was injected into volunteers, and plasma and urinary concentrations of the drug were determined by the radioactivity found in the colchicine zone on a thin-layer chromatographic system (*5*). Radioimmunoassay for colchicine (*6*) eliminates the need for an injected tracer and allows rapid analysis of small quantities of plasma or urine without purification. This assay should be of great use in toxicology, clinical pharmacology, and in the study of the physiology of microtubules (*7*).

Colchicine was conjugated to bovine serum albumin (BSA) through the ketone group on ring C by means of standard techniques (*8*). The only modification was an extraction with cold (4°C) chloroform to purify the colchicine oxime. Approximately 0.5 mg of the BSA conjugate was dissolved in 2.5 ml of saline and homogenized with 2.5 ml of complete Freund's adjuvant (Difco). Each of five New Zealand white rabbits received this mixture distributed among six subcutaneous injection sites at weekly intervals for 6 weeks, and then monthly. Binding of ^{3}H-labeled colchicine appeared in 6 weeks in one of the five rabbits; a usable titer appeared in 6 months. The colchicine-BSA conjugate was not characterized; the production of a usable antiserum was used as the end point of the procedure.

The radioimmunoassay depends on competition between unlabeled colchicine and ^{3}H-labeled-colchicine tracer for combination with binding sites on antibodies in the rabbit antiserum. Approximately 3000 dpm of ^{3}H-labeled colchicine (specific activity: 7.7 mc/mg, New England Nuclear) was used as the tracer. The tracer was dissolved in 0.5 ml of phosphate-buffered saline, *p*H 7.4, containing 0.01M EDTA and 0.01 percent merthiolate. From 5 to 200 μl of plasma, urine, or standard colchicine dissolved in control plasma or urine of the same volume as the unknown to be assayed was incubated for 24 hours at 4°C with the tracer and with 5 μl of rabbit antiserum, without agitation. The tubes were covered with aluminum foil to prevent exposure to ultraviolet light with the possible formation of varying quantities of the easily formed photoisomer lumicolchicine. The double antibody technique, in which we used 40 μl of sheep antiserum to rabbit γ-globulin and a second incubation of 16 hours at 4°C, resulted in reproducible separation of bound from free colchicine. After centrifugation, the supernatants containing the free colchicine were mixed with Aquasol (New England Nuclear), and the radioactivity was counted in a Packard Tri-Carb liquid scintillation spectrometer. A typical standard curve (Fig. 1) permitted measurement of from 0.05 to 10 ng of colchicine per assay tube. Within this range, there was complete parallelism between the standard curve obtained with authentic colchicine and dilutions of urine and plasma samples. Assay of more than 200 μl of urine or 300 μl of plasma resulted in significant deviation from parallelism, and such quantities were not used. A variety of biologically active alkaloids—such as atropine, nicotine, yohimbine, berberine, brucine, and emetine—showed cross-reactivity of less than 0.001 percent. Lumicolchicine, produced by ultraviolet irradiation of colchicine and characterized by thin-layer chromatography (*5*), showed a cross-reactivity of 0.68 percent. Recent data suggest that a portion of plasma colchicine is weakly bound to serum proteins (*9*). For the following reasons it is likely that our radioimmunoassay measures all of the colchicine in plasma. (i) Significant binding to plasma proteins would be reflected in a lack of parallelism between standard curves and dilutions of plasma samples, and (ii) methylene chloride extraction, which rapidly breaks protein-steroid complexes by denaturation, did not result in increased concentrations of plasma colchicine.

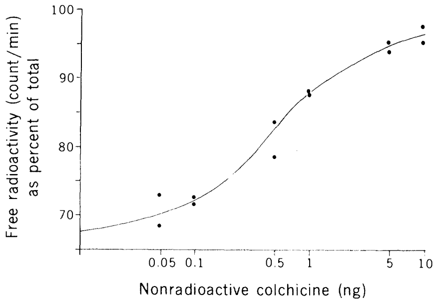

Fig. 1. A typical standard curve for the radioimmunoassay of colchicine.

Seven adult male patients between the ages of 45 and 66 years were studied (with informed consent). All patients had no evidence of hepatic or renal disease; one had a history of gout, but was on no medication, and another patient with a history of gout had a mild attack, with symptoms relieved by the colchicine used in the study. Colchicine (2 mg) was infused within 30 seconds into an antecubital vein in such a way that there was no infiltration into subcutaneous tissues. Blood was drawn into tubes containing dry heparin at 0, 1, 3, 5, 10, 15, 20, 30, 45, 60, 90, and 120 minutes. On the day of colchicine administration, urine was collected for the first 2 hours so that we could examine the acute excretory phase (*10*); collection was continued for the