Aug. 24, 1965 J. D. BROOKS ETAL 3,202,664

METHOD AND APPARATUS FOR DEALKYLATING AND HYDROGENATION OF ORGANIC COMPOUNDS

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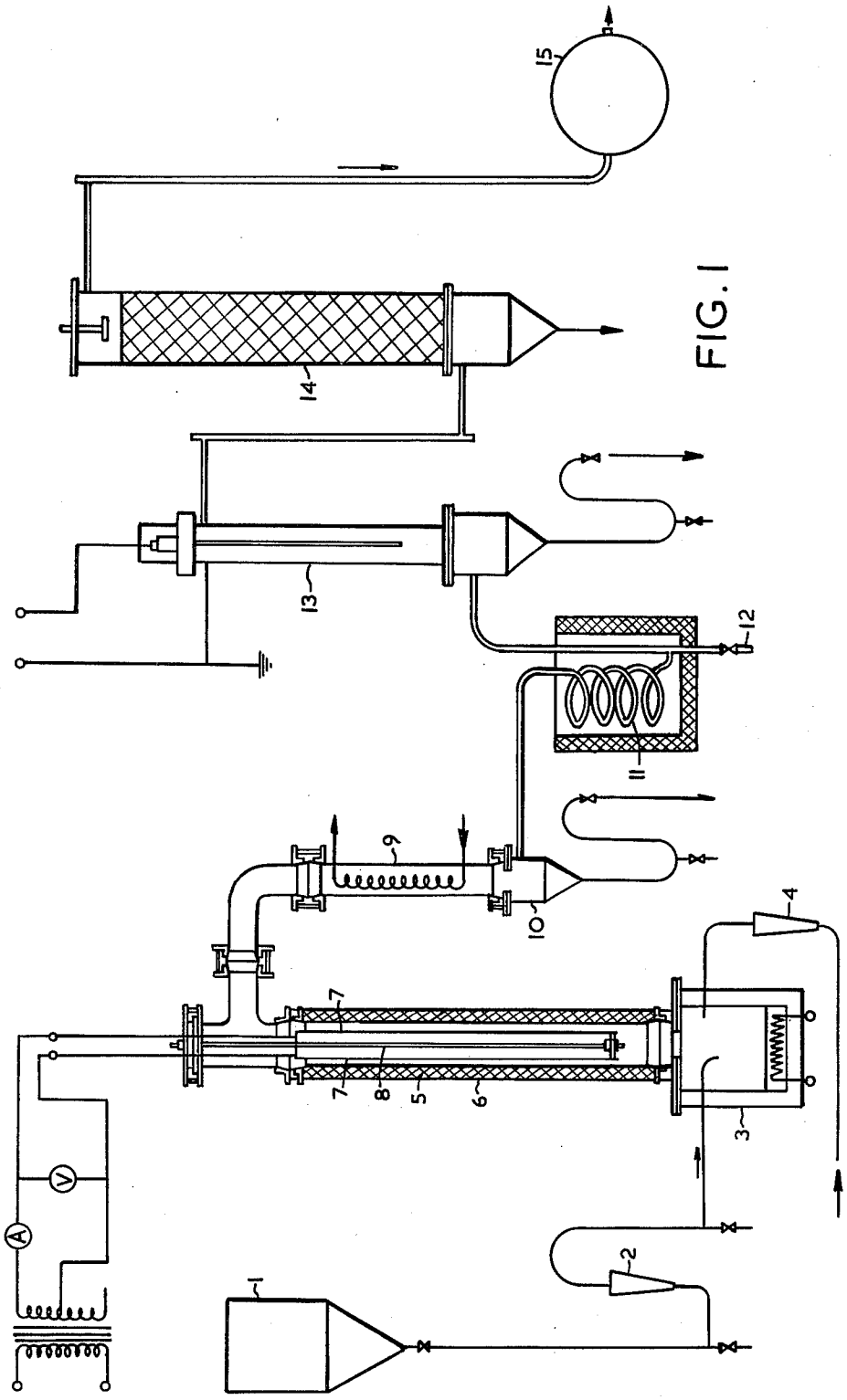
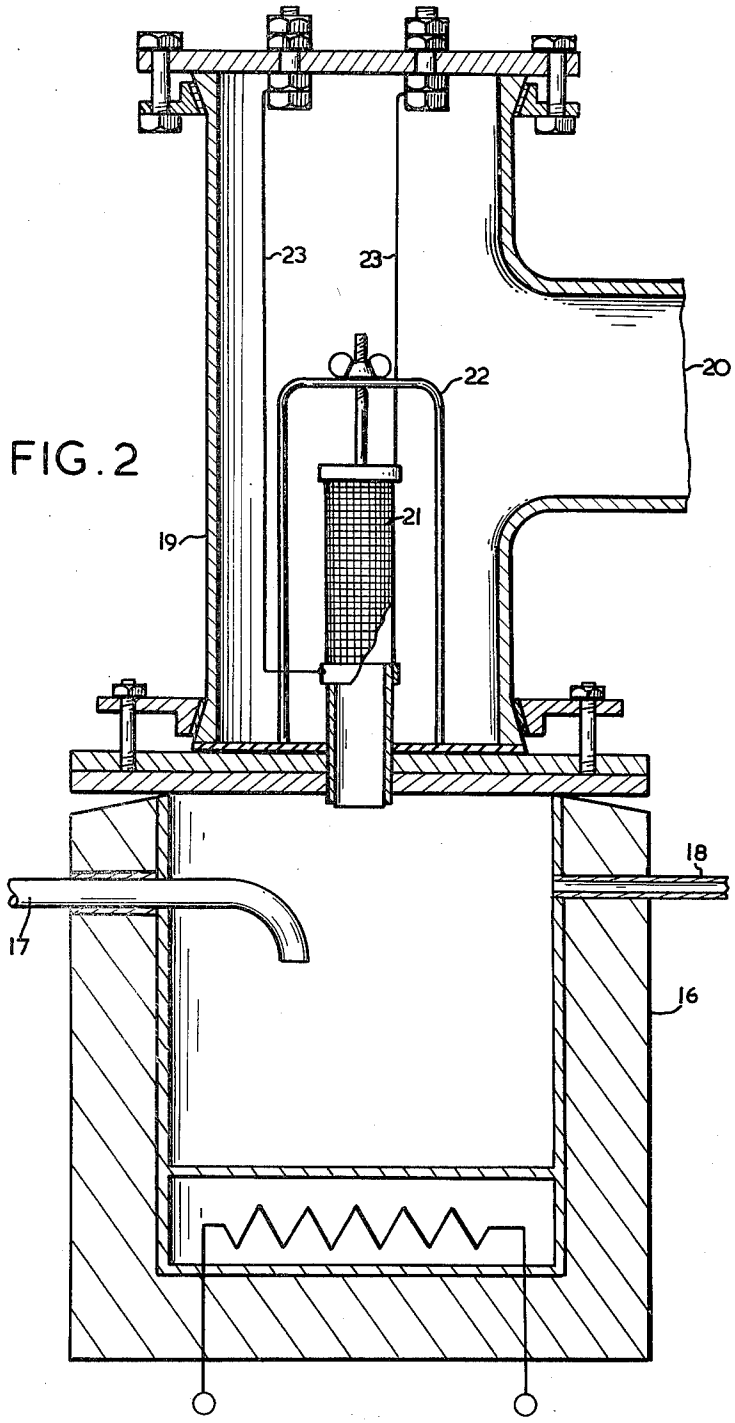


FIG. 1

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FIG. 2



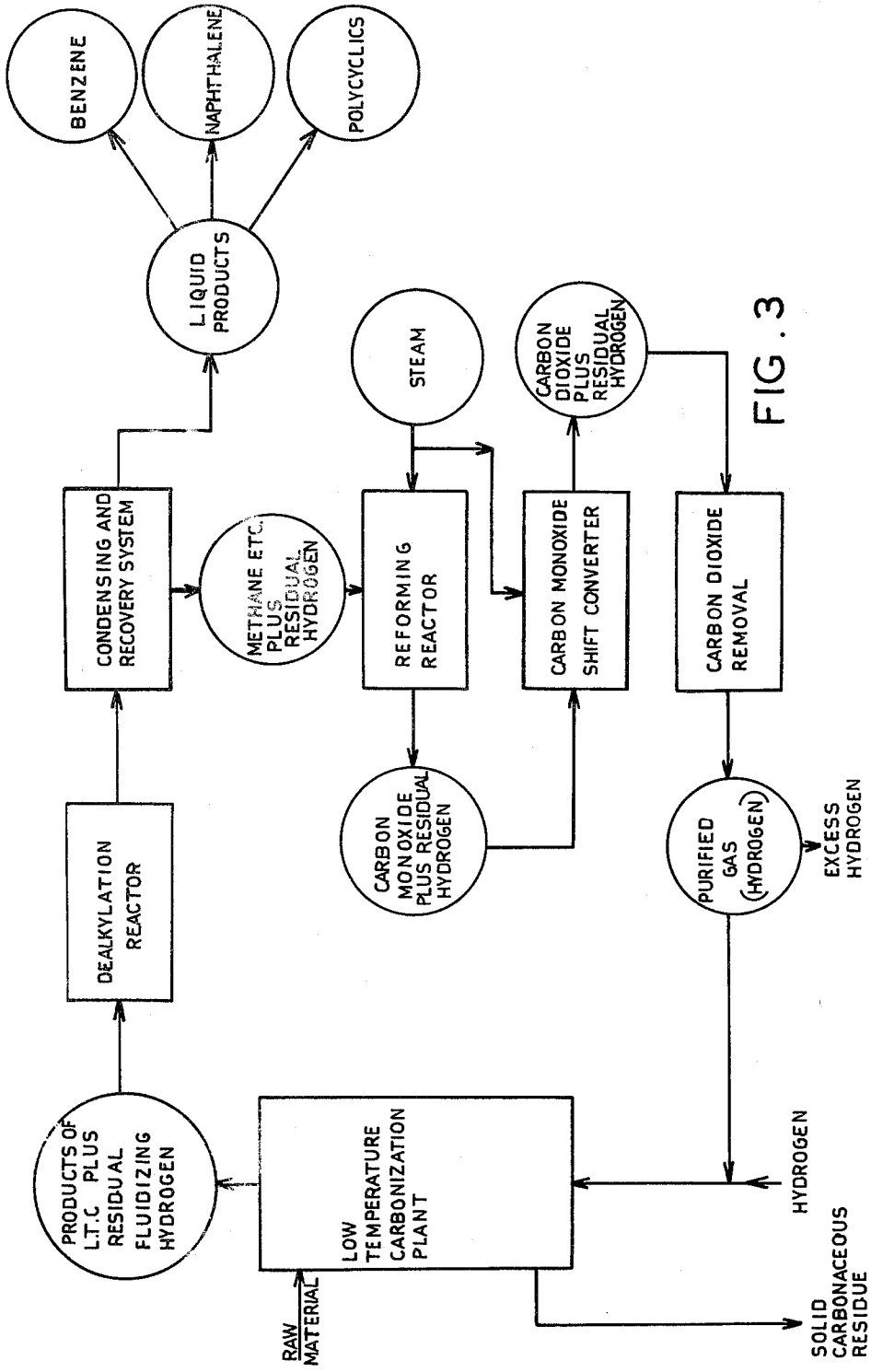

BENZENE
NAPHTHALENE
POLYCYCLICS
LIQUID PRODUCTS
STEAM
CARBON DIOXIDE PLUS RESIDUAL HYDROGEN
CONDENSING AND RECOVERY SYSTEM
METHANE ETC. PLUS RESIDUAL HYDROGEN
REFORMING REACTOR
CARBON MONOXIDE SHIFT CONVERTER
CARBON DIOXIDE REMOVAL
DEALKYLATION REACTOR
CARBON MONOXIDE PLUS RESIDUAL HYDROGEN
PURIFIED GAS (HYDROGEN)
EXCESS HYDROGEN
PRODUCTS OF L.T.C PLUS RESIDUAL FLUIDIZING HYDROGEN
LOW TEMPERATURE CARBONIZATION PLANT
HYDROGEN
RAW MATERIAL
SOLID CARBONACEOUS RESIDUE

FIG. 3

United States Patent Office

3,202,664

Patented Aug. 24, 1965

3,202,664

METHOD AND APPARATUS FOR DEALKYLATING AND HYDROGENATION OF ORGANIC COMPOUNDS

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Filed May 18, 1962, Ser. No. 195,799
Claims priority, application Australia, May 23, 1961, 4,980/61
7 Claims. (Cl. 260—290)

The present invention relates to the hydrogenation of relatively complex organic compounds and their mixtures in the vapour phase to achieve simpler compounds. The invention has particular application to the treatment of by-products from gas or coke production, oil refining, or other sources and also has wide application involving, for example, desulphurisation of organic compounds and substances.

The invention is based upon the discovery that organic materials when passed in the vapour phase together with hydrogen through a reaction vessel which contains a heated electrical resistance element undergo pyrolysis and/or destructive hydrogenation yielding products of simpler constitution.

In the case of by-products from gas or coke production which are complex mixtures of highly alkylated aromatic hydrocarbons, phenols and bases together with paraffinic and olefinic hydrocarbons and from which few industrially useful products can be easily isolated; valuable products can be simply and economically achieved with negligible formation of carbon or pitch. For example, benzene, naphthalene, phenol and pyridine, all of which have valuable industrial uses, are obtained from the different highly alkylated aromatic compounds mentioned above.

Additionally valuable gaseous products such as methane, ethylene and acetylene are produced and may be recovered. An important advantage of the invention is that tars may be treated in accordance with the invention in a vapourised condition directly from their source of production, intermediate handling being avoided.

By means of the invention it is possible to dealkylate alkyl aromatic compounds to give a very high yield of the parent aromatic compound, e.g. toluene is converted to benzene. Again straight chain compounds whether saturated or unsaturated may be converted to methane and other products.

By means of the invention it is also possible to dealkylate alkyl aromatic compounds and simultaneously to reduce the content of sulphur-containing impurities, these being converted, for example, to hydrogen sulphide and carbon disulphide. Furthermore the invention may be used to reduce the amount of sulphur-containing impurities in organic compounds which do not contain an alkyl group for example, commercial benzene with a relatively high content of sulphur-containing compounds may be refined in this way.

The effectiveness of the process is believed to be connected with the production of atomic hydrogen simultaneously with pyrolysis of organic compounds, providing an environment promoting dealkylation and other desired reactions.

It has been observed that in laboratory scale apparatus precautions were desirable to eliminate loss of atomic hydrogen by recombination of the hydrogen atoms on or

near the wall area of the reaction vessel. This requirement is not essential with preferred apparatus sufficiently large to avoid migration of hydrogen atoms to the wall region.

One method of application of the invention consists in passing vapourised organic materials together with hydrogen through a reaction vessel in contact with a heated electrical resistance element, maintained at temperatures between 1000° C.–1500° C., the issuing vapours being collected and separated into desired fractions. The process may be carried out at atmospheric or elevated pressures.

One form of the apparatus in accordance with the invention comprises a reaction vessel consisting of a tube either formed from or lined with a suitable heat resistant material (chemically inert under the conditions of reaction) through which extends one or more electrically heated tungsten or other suitable metal wires or a cylinder of platinum or other metal gauze located along or parallel to the longitudinal axis of said reaction vessel, the feed end of the reaction vessel communicating with sources of vapourised organic material and hydrogen and the outlet communicating with separation and storage facilities.

The following examples, utilizing laboratory scale apparatus consisting essentially of a glass tube of about 1" diameter and 8 ft. in length through which is extended a tungsten wire electrically heated to temperatures of the order of 1200° C., the said tube having an internal wall coating or metaphosphoric acid which serves to diminish loss of atomic hydrogen, show the application of the invention to simple organic compounds.

The materials passed through the reaction vessel were collected and identified as indicated in the following Table 1.

Table 1

Feed material:	Product composition
Toluene	92% benzene.
Meta-xylene	90% benzene. 8% toluene.
Para-xylene	87% benzene. 11% toluene.
1-methyl naphthalene	98% naphthalene.
Scrubber naphtha (Containing negligible quantities of benzene and naphthalene)	80% benzene. 10% naphthalene.
Ortho-cresol	47% benzene. 10% toluene. 15% phenol. 6% cyclopentadiene. 7% water. 3% naphthalene.
2,4 and 2,5-lutidine	5% hydrogen cyanide. 10% benzene. 20% pyridine. 30% methyl pyridines. 2% naphthalene.

The operational temperature and rate of flow are variable to suit the starting materials and desired end product or products. Optimum conditions in any given case may be determined by routine test procedures.

As an indication of the aspects of control of the process, it is pointed out that in dealkylating para or meta-xylene a flow rate of added hydrogen of 250 ml./minute using the previously described laboratory apparatus gave

benzene yields of 88 and 89% by weight. Doubling the flow rate reduced the yield by half and quadrupling it reduced the yield by more than a further half.

In general temperature control is predictable, too low a temperature giving poor conversion and too high a temperature giving rise to unwanted products e.g. condensation products such as diphenyl or in extreme conditions pitch and carbonaceous deposits.

It will be appreciated that the apparatus may be of any desired magnitude and will be constructed to suit operative conditions and quantities of materials to be handled.

The invention and more particularly its application to industrial uses will be more readily understood from the following description taken in conjunction with the accompanying drawings in which:

FIGURE 1 shows one form of dealkylation reactor and equipment for recovering the products of the reaction;

FIGURE 2 shows a modified form of the reactor illustrated in FIGURE 1, and

FIGURE 3 is a flow diagram showing how the apparatus in FIGURES 1 and 2 may be employed for the direct treatment of tars and organic vapours at their source of production.

As shown in FIGURE 1 the liquid material to be treated in accordance with the invention is contained in liquid feed tank **1** and passes through flow meter **2** into flash vaporizer **3**. The vaporized material then passes together with hydrogen (from flow meter **4**) into dealkylation reactor **5** which comprises an industrial Pyrex tube thermally insulated as shown at **6** and carrying four tungsten wires **7** on supporting rod **8**, the tungsten wires being heated by a controllable power supply. The product from the dealkylation reactor passes through water cooled condenser **9** and the liquid condensate collects in catch pot **10** whilst uncondensed products are passed through chilled condenser **11** from which further liquid condensate may be removed at **12**. The remaining vapours then pass through electrostatic precipitator **13** and finally through scrubbing tower **14** through which chilled wash oil is downwardly passed. The gases are passed through gas meter **15** and then collected.

FIGURE 2 illustrates a flash vaporizer **16** with liquid feed inlet **17** and hydrogen inlet **18**. The vaporous products from the flash vaporizer then pass through dealkylation reactor **19** and the products of the reaction leave the reactor and go to the recovery plant at **20**. The heating element in the reactor **19** comprises a platinum or other suitable gauze cylinder **21** held in place by bracket **22**, the cylinder being heated electrically via wire conduits **23**.

FIGURE 3 shows the treatment of tars from for example a fluidized bed carbonization unit. The tars together with the fluidizing gas containing hydrogen and with extra hydrogen if necessary pass through the dealkylation reactor, and the liquid products are condensed. The gases containing methane, ethylene and acetylene may be reformed by known methods to yield hydrogen and carbon dioxide. After removal of the latter by established procedures, the hydrogen is led back into the fluidized bed carbonization unit. In a continuous process excess hydrogen may be drawn off from the system.

The dealkylation process may be similarly operated in conjunction with other processes which yield alkylated aromatic compounds, for example processes employing petroleum-based feed stocks.

Examples of the treatment of industrial feed stocks are as follows:

Vertical retort tar naphtha, boiling range 190–210° C., containing saturated hydrocarbons (18%), olefinic hydrocarbons (14%) and aromatic hydrocarbons (65%, including naphthalene, 25%) gave a product (74% yield) containing benzene (31%) and naphthalene (66%).

Vertical retort tar middle oil, boiling range 200–290° C., containing saturated hydrocarbons (19%), olefinic hydrocarbons (20%) and aromatic hydrocarbons (61%) gave a product (40% yield) containing benzene (22%) and naphthalene (66%).

Acid-free low-temperature tar, of which 80% boiled below 400° C. gave a product (32% yield) containing benzene (25%), naphthalene (12%) and polycyclic hydrocarbons (62%).

Acid-free Lurgi tar gave a product (43% yield) containing benzene (15%) naphthalene (23%) and polycyclic hydrocarbons (57%).

Petroleum solvent A, containing 99.5% aromatic hydrocarbons, boiling range 165–215° C. gave a product (55% yield) containing benzene (53%) and naphthalene (13%).

Petroleum solvent B, 42% aromatic hydrocarbons, boiling range 210–280° C. gave a product (56%) containing benzene (26%) and naphthalene (50%).

Petroleum solvent C containing 82% aromatic hydrocarbons (33% naphthalene) boiling range 80–240° C. gave a product (57% yield) containing benzene (17%) and naphthalene (63%).

In the foregoing description where reference is made to hydrogen it is to be understood that hydrogen containing gases including coal gas, town gas or water gas are effective for the purposes of the invention.

What we claim is:

1. Process for dealkylating and hydrogenating gaseous by-product compounds from gas and coke production, said by-products comprising alkyl aromatic hydrocarbons, alkyl phenols, and alkyl aromatic bases admixed with paraffinic and olefinic hydrocarbons, comprising

(1) mixing said compounds in the gaseous state with molecular hydrogen,

(2) contacting the resultant gaseous admixture with metallic filament in a reaction zone while concomitantly maintaining said zone at a temperature sufficiently high to prevent condensation of organic vapors, said filament being heated to a temperature between 1000 and 1500° C., whereby atomic hydrogen is formed at said filament, and

(3) condensing the resultant dealkylated product.

2. Process for dealkylating and hydrogenating an admixture of alkyl cyclic compounds comprising

(1) mixing said compounds in the gaseous state with molecular hydrogen,

(2) contacting the resultant gaseous admixture with metallic filament in a reaction zone, while concomitantly maintaining said zone at a temperature sufficiently high to prevent condensation of organic vapors, said filament being heated to a temperature between 1000 and 1500° C., whereby atomic hydrogen is formed at said filament, and

(3) condensing the resultant dealkylated product.

3. Process for dealkylating an alkylated aromatic compound comprising

(1) mixing said compounds in the gaseous state with molecular hydrogen,

(2) contacting the resultant gaseous admixture with metallic filament in a reaction zone while concomitantly maintaining said zone at a temperature sufficiently high to prevent condensation of organic vapors, said filament being heated to a temperature between 1000 and 1500° C., whereby atomic hydrogen is formed at said filament, and

(3) condensing the resultant dealkylated product.

4. Apparatus for dealkylating and hydrogenating gaseous organic compounds comprising an insulated tubular reaction vessel, a plurality of bare metallic filaments extending longitudinally through said reaction vessel, means for injecting gaseous admixture into said vessel and means for withdrawing gaseous admixture from said vessel.

5. Apparatus of claim **4** wherein said vessel is lined with material chemically inert at temperatures of reaction.

6. Apparatus of claim **4** wherein said vessel is com-

posed of material chemically inert at temperatures of reaction.

7. Apparatus for dealkylating and hydrogenating gaseous organic compounds comprising an insulated tubular reaction vessel having an internal wall coating of metaphosphoric acid, metallic heating means extending longitudinally through said reaction vessel, said heating means capable of being electrically heated to temperatures of 1000 to 1500° C., means for injecting gaseous admixture into said vessel and means for withdrawing gaseous admixture from said vessel.

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