RUN NO. 2

FRACTION CARBON GASIFIED

ATOMS CARBON GASIFIED PER MINUTE PER ATOM CARBON IN BED

Fig. 5

Warren K. Lewis
Edwin R. Gilliland
Inventors

By Henry Kirk
Attorney
RUN NR. 3

FIG.-6

Warren K. Lewis  Inventors
Edwin R. Gilliland  By Henry Berk  Attorney
PRODUCTION OF PURE CARBON DIOXIDE
Application November 13, 1950, Serial No. 185,262
6 Claims. (Cl. 23—150)

1. This application is a continuation-in-part of U. S. Application Serial No. 92,812, filed May 12, 1949.

This invention relates to the production of pure carbon dioxide from oxidizable carbonaceous material, and particularly to the production of carbon dioxide free of inert gases, such as nitrogen. More particularly, the invention is concerned with the oxidation of carbonaceous material by means of solid oxidized copper as the source of oxygen.

At present there are two chief industrial sources of carbon dioxide, namely, as by-products from alcohol fermentation and as recovery from flue gases. The carbon dioxide produced in the former process is pure and cheap but limited in amount. The latter source requires absorption of the CO₂ in carbonate solutions followed by boiling to release the pure gas. This operation is perfectly workable but cumbersome and consumes very large quantities of heat. The amount of heat required for recovery of CO₂ from flue gas is so large that it is not uncommon to burn extra fuel over and above that necessary to make the CO₂. A cheap source of CO₂ is, therefore, highly desirable.

In the production of flue gas, the oxidizing agent generally employed is air. The use of air introduces into the product gas large amounts of inert gases, such as nitrogen, which complicate the concentration of CO₂ by condensation or absorption.

It is, therefore, the principal object of this invention to provide an improved process for producing pure carbon dioxide with the aid of solid oxidizing materials possessing the necessary oxidation potential as the oxygen transfer agent under controlled reaction conditions.

It is a further object of this invention to provide a process for the conversion of oxidizable carbonaceous material, particularly, finely-divided coal and coke to carbon dioxide.

A more specific object of this invention is to provide a process of the type specified which will permit oxidation of the carbonaceous material by oxidized copper, without contaminating the carbon dioxide with inert gases, such as nitrogen.

It is also an object of this invention to produce carbon dioxide under pressure, thus minimizing the problems of compressing the carbon dioxide.

These and other objects of the invention will be apparent from the description to follow.

The source of carbon from which the carbon dioxide is prepared may be any oxidizable carbonaceous material, such as charcoal, coal, coke, heavy distillate oil, residual oils, gaseous hydrocarbons such as methane, natural gas, etc., peat, shale, oil sands, lignite, bitumen, etc. Charcoal and coke are the preferred solid starting materials, particularly coke and charcoal of low ash content. Charcoal fines and coke breeze are particularly suitable. Methane and natural gas are the preferred gaseous raw materials. The processes utilize raw material which in other processes suffer particular disadvantages.

The solid oxygen carrier employed in place of air in accordance with this invention is oxidized copper by which term is meant CuO, Cu₂O, mixtures of CuO and Cu₂O and the normally solid solutions of CuO and Cu₂O. Depending upon the temperature employed in the oxidation reaction it may or may not be necessary to employ a carrier for the copper oxide. Carbonaceous materials will react with oxidized copper at temperatures in the range of 400–1000°C. However, temperatures in the range of 800–1000°C are preferred with solid carbonaceous materials such as coke and charcoal, while with gaseous raw materials such as methane and natural gas lower temperatures in the range of 400–900°C are preferred. At the higher temperatures, i.e. 800–1000°C, copper oxide sinters and therefore it is used with a carrier such as Alumina, silica gel, kieselguhr, etc. When oxidizing CH₄ with oxidized copper, however, lower temperatures are satisfactory. At these lower temperatures sintering does not occur and the carrier can be dispensed with. Yet even in this instance the presence of a certain amount of inert carrier solid, e.g. sand, can assist the operator materially from a fluidization standpoint, even though the copper does not reside in the grain of the solid itself as in silica gel. Broadly, two types of carriers can be employed: (1) materials such as Alumina or silica wherein the copper oxide may become incorporated into the grain of the carrier, and (2) materials superactive as fluidizing assistants, e.g. clay, non-fused alumina powder, spent clay catalyst from petroleum oil treatment, kieselguhr, magnesia, etc.

The solid oxidized copper may be employed in a finely-divided form and contacted with the carbonaceous raw materials either in the form of a fluidized mass or a moving bed. The carbonaceous raw materials when solid are likewise used in a finely-divided state or as a moving gravitating bed.

The fluidized state of the solid reactants affords effective contact between the solids, ideal tem-
perature control and greatest uniformity of re-
actant distribution throughout the fluidized mass.
As a result the process is extremely flexible and
may be readily controlled at the desired degree
of carbon oxidation. Since the only oxygen avail-
able in the reaction zone is bound in the form of
a copper oxide, the product remains free of inert
gases, such as nitrogen.
In order to obtain proper fluidization all solid
reactants, both carbonaceous material and cop-
eroxide, should be ground to a size that sub-
stantially all of it will pass through 100-mesh
screen. For the best results, the ground solids
should be about 50% in the 50-mesh fraction, rang-
ing upwardly from about 20 microns to about
100-mesh with a large proportion of the mate-
rial between about 100- and 200-mesh.
Fluidization is accomplished in the carbon di-
oxide generator by means of carbon dioxide va-
pors produced in the reaction zone or separately
introduced therein. A portion of the CO2 prod-
uct is recycled to a lower portion of the reacting
solids to assure fluidization over their entire
height. Superficial linear flow velocities of the
fluidized gases within the fluidized bed may vary
between about 0.5 and 4 ft. per second for proper
fluidization of most practical solid reactants in
the particle sizes mentioned above.
Spent solid copper oxide is intermittently or
continuously reoxidized with air in a separate re-
sactor and returned stripped of air and combus-
tion gases and fluidized by CO2 to the CO2 gen-
eration zone. The spent oxygen carrier pref-
erably consists principally of copper contami-
nated with unreacted CuO and Cu2O, depending
upon the extent of oxidation in the CO2 gen-
erator. This mixture is conducted from the CO2
generation zone and contacted in the fluidized
state with air in a combustion zone to be re-
oxidized principally to CuO which is thereafter
returned to the CO2 generation zone. Since the
reoxidation reaction in the burner is highly exo-
thermic, all or at least a substantial part of any
heat required to bring the carbonaceous mate-
rial to reaction temperature is supplied to the
carbon dioxide generator in the form of sensible
heat of reoxidized copper oxide.
It has been found that carbonaceous materials
will react with copper oxide at temperatures in
the range of 400° C. to 1000° C., preferably
700°-1000° C., to form CO and copper oxide.
Coke reacts with retort coke at temperatures as low
as 800° C. but preferably in the range of
800-950° C., for desired reaction rates. Reaction
between CuO and wood charcoal is satisfactory
at about 700° C., while methane reacts with CuO
alone or supported on silica gel or Alundum, etc.
at temperatures as low as 400° C. Successful
production of CO2 has been achieved by reacting
methane with CuO (without a carrier) at tem-
peratures in the range of 800° C. to 850° C. but
an upper limit of 900° C. is preferred for this
system. One can operate at temperatures below
800° C. but reaction rates fall off appreciably. In
all instances the upper temperature limit to be
employed is governed by the sintering tempera-
ture of the copper oxide. For this reason tem-
peratures above about 1000° C. are to be guarded
against if not avoided altogether.
The reaction may be carried out in a two-vessel
or three-vessel system employing fluidized solids,
or the reaction may take place in a moving-bed
or soaker-type reactor.
The reoxidation of the spent copper oxide
may be carried out, while avoiding sintering, at
375

temperatures in the range of the reaction tem-
peratures, i.e., not above about 1000° C.
In order to assure high reaction rates and to
carry carbon oxidation in the CO2 generator as
far as possible, it is preferable to employ a sub-
stantial stoichiometric excess of copper oxide over
the oxidizable carbon present. Even if there
should be an unconversion of the carbon oxida-
generator, the production of carbon monoxide there-
from will be negligible. Any carbon monoxide
formed reacts rapidly with copper oxide to pro-
duce CO2, but the carbon reacts only slowly
with the CO2 thus produced at the temperature in
the generator. In other words, the carbon will
not react rapidly enough with the CO2 produced
in order to form CO in serious amounts.
The nature of the present invention will appear
more clearly from the following detailed descrip-
tion of the accompanying drawings in which each
figure is a front elevation in diagrammatic form
of one type of plant apparatus suitable for the
practice thereof.
Figure 1 represents a two-vessel system em-
ploying fluidized solids. The system is adaptable
to any form of carbonaceous material.
Figure 2 represents the moving-bed or soaker-
type reactor employed with solid carbonaceous
materials.
Figure 3 represents a system employing alter-
nate moving beds of solid carbonaceous material
and copper oxide.
Referring to Figure 1, numeral 1 represents a
carbon dioxide generator into which finely-
divided carbonaceous material, such as coke, is
fed from hopper 2 via line 3. To aid in the flow
of the carbonaceous material into vessel 1 a small
amount of an aerating gas, such as carbon di-
oxide, may be added through line 4. Numerals
5 and 6 represent a hopper containing finely-divided
solid copper oxide. The finely-divided oxide en-
ters an upper portion of oxidation zone 7 via line
8. In initiating the process hot combustion
gasses from an auxiliary source (not shown) are
introduced into vessels 1 and 4 and then, while
continuing to be supplied with hot gases, copper oxide is
added to vessel 1 until the vessel is properly
charged and the oxide heated. The hot oxide
collects in withdrawal well 24 and is withdrawn
from vessel 1 and passed under the pseudo-
hydrostatic pressure in a fluidized condition via
line 9 into generator 1, preferably at an upper
level. In generator 1 a temperature of 800° C.
to 1000° C., preferably 900° C. to 950° C., is main-
tained. When feed of coke through line 3 is in-
terminated, reaction occurs between the coke and cop-
er oxide forming CO2 at the prevailing reaction
temperature.
The ratio of the rate at which carbonaceous
feed should be fed to vessel 1 relative to the rate
of feed of copper oxide to the same vessel is de-
termined primarily by the chemical reactivity
of the carbonaceous material. Thus, if one uses
ordinary retort coke as the feed through line 3, in
order to get satisfactory capacity of CO2 produc-
tion from reactor 1, the coke must be fed in large
stoichiometric excess over the oxygen available
in the entering copper oxide. This does not mean
that all the oxygen of the copper oxide will be
consumed in vessel 1. The remainder of the
coke, relative to the oxide, must be controlled so
that there is unreduced copper oxide in the solids
leaving through line 17. Along with this oxide,
however, will be found a considerable amount of
unreacted coke. This coke will be consumed in
vessel 1, markedly increasing heat generated
there. If, however, the carbonaceous material employed is a highly active wood carbon or a material such as methane, in order to maintain at least a small amount of residual copper oxide in the effluent solids from 1, the ratio of carbonaceous feed to oxygen in the oxide will be far lower than in the case of coke and, particularly in the absence of carbonaceous material such as methane, which will be introduced at the bottom of 1, it will be less than the stoichiometric amount.

In operating, using finely-divided coke as the carbonaceous material and CuO on silica gel as the oxidizing agent, generator 1 contains above grid 35 a fluidized mass consisting substantially of CuO introduced via line 9 at a point above the uppermost tray 43 and overflowing through overflow weirs 44 to the lower trays 43. The oxide has a particle size generally of 100 to 300 mesh. The temperature of the oxide in the generator is held at about 800°C to 1000°C. The temperature control of the exothermic reaction occurring in the generator 1 is effected in one alternative by means of a cooling medium circulating in the cooling coils 33 located on one or more plates of the vessel 1.

The generator unit is best started up, as previously related, by introduction into the bottom thereof of hot combustion gases for both fluidization and heat supply. When the temperature is brought up sufficiently so that active interaction of the coke and copper oxide will set in, recirculate of cooled top gas from vessel 1 to the bottom of the vessel for fluidization is started and coke introduced. This soon purges gases other than CO2 from the unit. However, external CO2 may, if desired, be introduced to expedite the purging and fluidization. In order that the carbon contained in the coke be substantially converted to CO2 a staged system is provided. For this purpose generator 1 contains trays, bubble plates, or other staging device 43 provided with overflow levels or downcomers 44 at intervals throughout the vessel 1. The number of trays, etc. may be varied according to the production capacity desired of the vessel and the extent of the oxidation required. Although staging has been illustrated by the use of trays and downcomers, any manner of minimizing the mixing of solids entering and leaving the generator may be employed. The fluidized materials entering the generator through lines 3 and 9 build up on the tray until the level of the overflow is reached, after which the fluidized materials pass downwardly in succession to the next lower level. The depth of the bed on the tray is preferably about 2 to 3 feet. The flow of fluidized materials occurs countercurrent to the upward flow of fluidizing gas entering the vessel through line 31. However, the flow rate of the gas is controlled so as not to interfere with the overall downward flow of the fluidized solids.

Substantially pure CO2 amounting to as much as 0.9 mol. per atom of carbon in the coke charged and containing suspended solids is withdrawn overhead from generator 1, passed through cyclone 10 and cooled in cooler 11 substantially free of entrained solids. The recovered gas is further worked up by compression and/or absorption by conventional means not shown. Solids separated in cyclone 10 may be returned to the fluidized mass through pipe 42. Particles of undesirable small size or excess may be discarded through line 13.

Part of the CO2 produced is removed from line 11 via line 14 and introduced after cooling into the bottom of generator 1, with the aid of blower 45 to maintain fluidized conditions throughout the solids in the generator. Purge lines 15 and 16 equipped with valves are provided to introduce purge gas, such as CO2 into line 9, freeing the solid phase flowing therethrough of excess air and combustion gases. The energy required to lift the purged solid into vessel 1 is supplied by means of CO2 intrinsic to the system.

The spent solids contained in vessel 1 are removed at a rate which will secure the oxidation of the coke to CO2 in vessel 1 to the proper point. They are then passed under the pseudo-hydrostatic pressure of the fluidized mass through withdrawal well 47 and are mixed with the assistance of dilution air entering through line 48 and carried into an upper portion of regenerator 1 via line 19. Additional aeration gas may be supplied through lines 32 and 34. Standpipe 17 may be enlarged in area so as to serve as a soaker in order to more completely remove carbon from the withdrawn solids. The solid material thus removed contains reacted copper oxide in the form of Cu, CuO and some unconverted CuO, carbon, and ash. The amount of carbon carried out through line 11 into regenerator 1 depends upon the reactivity of the carbon toward copper oxide, which depends largely upon the character of the carbonaceous material. However, the amount of carbon leaving generator 1 is preferably low, for example, about 0.1 to about 1 weight percent of the fluidized copper oxide recycled to the regenerator. By and large, the more carbon put through generator 1, other operating conditions unchanged, the more CO2 is produced; however, the more carbon must be burned in regenerator 7. Where the demand for pure CO2 is equivalent to only a limited fraction of the carbon in the fuel, which must still get heat required for other processes, as in a boiler plant, running high carbon content in generator 1 can be very advantageous. Thus, even using a highly inert reagent coke of low reactivity, by carrying about 5% of carbon in the oxide leaving generator 1, one can reduce over a third of a ton of pure CO2 per day per square foot of cross section in that unit with a net bed depth in it of 40 feet, at atmospheric pressure and an operating temperature of 1000°C. Even with no staging in vessel 1, about 25% of the carbon in the fuel is obtained in the form of CO2 from generator 1, the rest being used for heat production in 7. The heat is recovered in coil 28, which functions best as the water tubes of a boiler. With more reactive carbons one can operate generator 1 at lower temperatures, secure larger productions of CO2 from it, reduce its height, recover for higher fractions of the fuel as pure CO2 from vessel 1, or combine these advantages as seems most desirable under any specific set of circumstances.

High ash content carbonaceous material causes rapid build up of ash in the copper oxide to be recycled and this ash build up is not desirable. This ash may be removed, e.g., by conventional ash-electrostatic precipitator 18, and gas withdrawn continuously from line 30 by insertion of the separating equipment in line 20. In either case the recovered copper oxide is returned to the system through feed mechanism 5.

The hot gases emerging from regenerator 1 via line 20 are sent to the waste heat boiler system. In regenerator 1 the carbon carriers over from generator 1 are burned with air entering predominantly through line 21 and the spent copper ox-
ide becomes reoxidized predominantly to CuO. A temperature of 800°C to 1000°C is maintained in regenerator 7 and the reaction proceeds according to the equation: 2CuO + O₂ → 2CuO.

The superficial linear gas velocity within the regenerator 7 is preferably maintained at about 0.5 to 3.0 ft. per second to establish an apparent bed density up to about 70 to 80 lbs. per cubic ft. for unsupported metal oxide and a bed height between grid 22 and level 23 of about 5 to 15 ft.

The reoxidized copper oxide is withdrawn under the pseudo-hydrostatic pressure of the fluidized mass via withdrawal well and standpipe 24, and returned to generator 1 via line 8 entering near the top thereof. Aerating lines 15, 18, and lift line 25 equipped with valves are provided for introduction of purge and fluidizing gas respectively such as CO₂ or steam to strip and lift the solid phase to vessel 1 where the cycle is repeated. Carbon dioxide introduced through lines 15 and 18 serves to purge the fluid of any remaining traces of nitrogen and air which may be contained therein, as it is desirable to keep all but traces of nitrogen from generator 1. Hot spent gases containing excess air, nitrogen, etc. are removed from regenerator 7 and are withdrawn from the system and sent to waste heat recovery.

The maximum temperature which can be employed anywhere in the system is that set by the tendency of the recycling solids to sinter. This is influenced by the impurities, e.g., the composition of the ash of the fuel actually used. Consequently, this maximum allowable temperature must be determined for the case in hand. Once it is so determined, the operation must be controlled to keep within this limit. Thus, the combustion in vessel 7 generates a large quantity of heat. The temperature in that vessel must be kept down by controlling operation of cooling coil 26, or preferably by controlling solid circulation rate through solid cooler 39. In the latter case a portion of hot solids is withdrawn from vessel 7 via withdrawal well and standpipe 23 and conveyed with the assistance of lift gas, preferably air entering through pipe 30, through solid cooler 39 operating as a waste heat boiler. The cooled solids are returned to vessel 7 through line 40. Heat is also evolved in vessel 1. The temperature may be controlled by coils 33, but, alternatively, if vessel 7 is operated at a temperature somewhat below that at the outlet of vessel 1 and sufficient solids be recycled through the system, the use of coil 33 may be dispensed with. It is within the scope of this invention to add to the copper oxide entering generator 1 a small amount of other solid materials such as alkaline carbonates and oxides which catalyze the reaction in generator 1. Even inert solid heat carriers may be added.

Withdrawal wells and standpipes 17 and 24 in vessels 1 and 7 respectively are located as far as possible from the end of the standpipes supplying the charges to the respective vessels. Vessels 1 and 7 are provided with cyclone separators 10 and 27 for removal of finely-divided material from the outgoing gases, such as copper oxide or carbon fines and ash. The cyclone separators are equipped with hoppers for receipt of solids to the dense bed. Materials which are too small in size to remain fluidized are withdrawn via lines 13 and 23 respectively. This material will also contain some ash produced in the system. Any fly ash not retained by the separators can be removed from the gas streams leaving the vessels through lines 11 and 30 respectively by suitable means, such as scrubbing, if desired.

The fluidized solids in vessels 1 and 7 are maintained at an apparent density which may go up to 70 to 80 lbs. per cubic ft. When a carrier is employed with the copper oxide the apparent density approaches the lower value. Once the process is in operation the only additional copper oxide required is make-up material to supplement that which becomes too fine to fluidize or which is lost by dilution with ash.

The system described may be operated at atmospheric or superatmospheric pressure. It is preferred to operate the generator under superatmospheric pressure and the regenerator under atmospheric pressure.

The apparatus described in Figure 1 is also ideally suited for the conversion of gaseous and gasifiable hydrocarbons to CO₂. Such hydrocarbons, e.g., methane, may be introduced into vessel 1 via line 38 controlled by valve 37. The hydrocarbon gas passes upwardly through grid 35 and contacts the copper oxide. In this case counterflow of solids and gas in vessel 1, though still desirable, is unnecessary and bed depth in generator 1 can be as low as 20 ft. However, it is very desirable to maintain a considerable excess of CO₂ through vessel 1 relative to the CH₄ fed to assure the presence of CuO throughout the bed and in the solids effluent from it. At the temperature of the copper oxide the hydrocarbon reacts with it to produce CO₂ and H₂O which emerge from vessel 1 via line 11. The water is removed from the CO₂ by conventional means not shown.

Solids circulation between vessels 1 and 7 may also be accomplished by arranging the vessels at different levels and using standpipes and dilute solids in gas suspensions to accomplish downward and upward flow respectively in a manner known in the art of fluid solids handling.

It will be understood that the gases used for fluidizing the various solids in transfer lines and for purging purposes, should be selected as not to interfere with the reactions intended, for example, air may be employed as a fluidizing means supplied in lines 15, 32 and 34. However, carbon dioxide, steam, CO, Hz, water gas or methane is used as the fluidizing gas in lines 15, 18, 23 and 31. Gas from these sources is supplied solely of the elements carbon, hydrogen, and oxygen and are all converted under the reaction conditions in generator 1 to CO₂ and/or water vapor. Air or nitrogen is not to be used as the fluidizing gas at the latter points since it is not desirable to contaminate the CO₂ product with nitrogen.

While a two or more vessel system of the type illustrated is essential for a continuous production of CO₂, it is noted that intermittent operation carried out in a single vessel in a "make and blow" manner is likewise within the scope of the present invention. In this case the "make" period will be operated substantially at the conditions outlined above for generator 1 and the "blow" period at those conditions outlined for regenerator 7 as will be readily understood by those skilled in the art.

Figure 23 illustrates a diagrammatic sketch of apparatus employed in carrying out the process with the soaker-type or moving bed reactor. Referring to Figure 2, numeral 1 represents a reaction vessel to the upper end of which are added carbonaceous solid via line 2 and hot copper oxide, e.g., CuO, via line 3. It is also possible to mix the two solids before introduction into vessel 1.
The solids are allowed to fill the vessel and thereafter flow through the vessel at a predetermined rate controlled by the operation of valve 9. The solids undergo reaction during passage downwardly in the vessel 1 according to the equation: C+4CuO→CO₂+2Cu₂O. The CO₂ generated passes up through the solids and is removed via line 4. In vessel 1 the solids settle at a predetermined rate without turbulence or with only a minimum amount of turbulence. To assure complete conversion of carbon provision is made for the introduction of small amounts of CO₂ gas into the bottom of the reaction vessel from line 4 via line 7 and pump 8. The reduced copper oxide is removed from vessel 1 via line 8 at a predetermined rate and is conveyed to a regenerator not shown by the assistance of aerating gas such as air introduced via line 6. The regeneration operation and return of reoxidized solids to line 3 is the same as described in connection with Figure 1.

Figure 3 represents the alternate bed type of reactor. In Figure 3 alternate beds of copper oxide contained in oxide chambers 1 are superimposed upon beds of carbonaceous solids such as charcoal contained in carbon chambers 2, etc. In initiating the processes each of the oxide chambers 1 is filled with hot copper oxide entering the uppermost chamber via line 1 and passing via line 1 to the next lowermost chamber, etc. Similarly the solid carbonaceous material enters uppermost carbon chamber 2 via line 6 and proceeds to flow downwardly via line 5 until each of the carbon chambers contains the desired level of carbonaceous material. When the process has been initiated copper oxide and carbonaceous solid are fed to the respective chambers at a uniform rate determined by the rate of withdrawal of the solids from the lowermost carbon and oxide chambers respectively. In starting up the process CO₂ is produced in the lowermost oxide chamber, e.g. by passing a mixture of CO and CO₂ via line 3 into the lowermost oxide chamber 1. Or, charcoal may be reacted with an excess of copper oxide in the lowermost oxide chamber. The gases pass upwardly through the oxide bed during which passage the CO is converted substantially to CO₂. The CO₂ stream is taken off the oxide chamber via line 4 and is introduced into the bottom of the lowermost carbon chamber 2. The CO₂ passes upwardly through the bed of carbonaceous material and is reacted to a mixture of CO and CO₂ by the reaction:

\[
\text{CO} + \text{C} \rightarrow 2\text{CO}
\]

This mixture of CO and CO₂ is withdrawn via line 12 and is introduced into the bottom of the next lowermost oxide chamber whereby the cycle is repeated. As many pairs of alternate beds may be employed as desired. The final CO₂ product is withdrawn via line 5 overhead from the uppermost oxide bed thus assuring the absence of CO in the final product. Spent copper oxide is withdrawn from lowermost oxide chamber via line 8 and sent to a regenerator as described in connection with Figure 1. The hot regenerated copper oxide is re-introduced into the reaction system via line 9. A continuous supply of carbonaceous material is furnished to the system via line 6, and any unreacted carbon from the lowermost carbon chamber is withdrawn via line 15 and returned via line 10 to supply line 6. Ash build-up is prevented by periodic withdrawal of part of the carbon via line 13. In the system described in Figure 75.

---

### Run No. 1

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>Average temp. (^{°}\text{C.})</th>
<th>CO₂ percent</th>
<th>O₂+CO₂ percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>884.3</td>
<td>68.33</td>
<td>2.21</td>
</tr>
<tr>
<td>2.5</td>
<td>884.14</td>
<td>68.37</td>
<td>2.29</td>
</tr>
<tr>
<td>5.0</td>
<td>884.17</td>
<td>68.37</td>
<td>2.35</td>
</tr>
<tr>
<td>7.5</td>
<td>884.19</td>
<td>68.43</td>
<td>2.30</td>
</tr>
<tr>
<td>10.0</td>
<td>884.21</td>
<td>68.68</td>
<td>2.30</td>
</tr>
<tr>
<td>12.5</td>
<td>884.22</td>
<td>68.70</td>
<td>2.21</td>
</tr>
<tr>
<td>15.0</td>
<td>884.24</td>
<td>68.35</td>
<td>2.21</td>
</tr>
<tr>
<td>17.5</td>
<td>884.27</td>
<td>68.33</td>
<td>2.18</td>
</tr>
<tr>
<td>20.0</td>
<td>884.30</td>
<td>68.29</td>
<td>2.14</td>
</tr>
<tr>
<td>22.5</td>
<td>884.32</td>
<td>68.24</td>
<td>2.15</td>
</tr>
<tr>
<td>25.0</td>
<td>884.33</td>
<td>68.09</td>
<td>2.10</td>
</tr>
</tbody>
</table>

---

### Run No. 2

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>Average temp. (^{°}\text{C.})</th>
<th>CO₂ percent</th>
<th>O₂+CO₂ percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>907.84</td>
<td>58.4</td>
<td>1.65</td>
</tr>
<tr>
<td>2.5</td>
<td>907.61</td>
<td>58.3</td>
<td>1.63</td>
</tr>
<tr>
<td>5.0</td>
<td>907.55</td>
<td>58.3</td>
<td>1.58</td>
</tr>
<tr>
<td>7.5</td>
<td>907.48</td>
<td>58.2</td>
<td>1.53</td>
</tr>
<tr>
<td>10.0</td>
<td>907.45</td>
<td>58.2</td>
<td>1.46</td>
</tr>
<tr>
<td>12.5</td>
<td>907.41</td>
<td>58.0</td>
<td>1.38</td>
</tr>
<tr>
<td>15.0</td>
<td>907.36</td>
<td>57.9</td>
<td>1.29</td>
</tr>
<tr>
<td>17.5</td>
<td>907.32</td>
<td>57.8</td>
<td>1.21</td>
</tr>
<tr>
<td>20.0</td>
<td>907.29</td>
<td>57.7</td>
<td>1.15</td>
</tr>
<tr>
<td>22.5</td>
<td>907.26</td>
<td>57.6</td>
<td>1.09</td>
</tr>
<tr>
<td>25.0</td>
<td>907.23</td>
<td>57.5</td>
<td>1.05</td>
</tr>
</tbody>
</table>

---

### Run No. 3

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>Average temp. (^{°}\text{C.})</th>
<th>CO₂ percent</th>
<th>O₂+CO₂ percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>908.84</td>
<td>58.5</td>
<td>1.67</td>
</tr>
<tr>
<td>2.5</td>
<td>908.61</td>
<td>58.4</td>
<td>1.65</td>
</tr>
<tr>
<td>5.0</td>
<td>908.55</td>
<td>58.3</td>
<td>1.63</td>
</tr>
<tr>
<td>7.5</td>
<td>908.48</td>
<td>58.2</td>
<td>1.58</td>
</tr>
<tr>
<td>10.0</td>
<td>908.45</td>
<td>58.2</td>
<td>1.53</td>
</tr>
<tr>
<td>12.5</td>
<td>908.41</td>
<td>58.0</td>
<td>1.46</td>
</tr>
<tr>
<td>15.0</td>
<td>908.36</td>
<td>57.9</td>
<td>1.38</td>
</tr>
<tr>
<td>17.5</td>
<td>908.32</td>
<td>57.8</td>
<td>1.29</td>
</tr>
<tr>
<td>20.0</td>
<td>908.29</td>
<td>57.7</td>
<td>1.21</td>
</tr>
<tr>
<td>22.5</td>
<td>908.26</td>
<td>57.6</td>
<td>1.15</td>
</tr>
<tr>
<td>25.0</td>
<td>908.23</td>
<td>57.5</td>
<td>1.09</td>
</tr>
</tbody>
</table>

---

### Remarks

Run No. 1: Temperature: 895° C. to 906° C.; pressure in generator: 1.171 atm. (aver.); superficial velocity: 0.205 ft/sec.

Run No. 2: Temperature: 906° C. to 906° C.; pressure in generator: 1.095 atm. (aver.); superficial velocity: 0.270 ft/sec.

Run No. 3: Temperature: 895° C. to 895° C.; pressure in generator: 1.105 atm. (aver.); superficial velocity: 0.236 ft/sec.
These are batch runs, data of which are more informative as to the characteristics of the reactions. The weight percent copper, expressed as metal, in the impregnated gel at the start of the runs was 12.2% The bed densities were about 21 pounds per cubic foot, an account of the nature of the carrier. The initial charges are shown in the following table.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Lbs. carbon per cu. ft. bed</th>
<th>Lbs. available oxygen per cu. ft. bed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run No. 1</td>
<td>1.22</td>
<td>0.422</td>
</tr>
<tr>
<td>Run No. 2</td>
<td>0.622</td>
<td>0.378</td>
</tr>
<tr>
<td>Run No. 3</td>
<td>2.22</td>
<td>0.506</td>
</tr>
</tbody>
</table>

The net CO₂ synthesis rates for Runs 1, 2, and 3 are shown respectively in Figures 4, 5, and 6. The high initial rates, which, however, fall off rapidly, are believed to be due to the fact that copper oxidized high in oxygen (down to an atomic ratio of O/ Cu of about 0.7 to 0.8) exert a higher partial pressure of oxygen than oxides containing less oxygen. There follows a period of quite constant rate, but the rate again starts to drop in the neighborhood of an O: Cu ratio of about 0.5. Beyond this point also the CO content of the gas starts to rise sharply.

At the start of the plateau of Figure 4 (Run No. 2), the net production rate of CO₂ was 2.87 cu. ft. (measured at standard conditions) per hour per cu. ft. of bed. This figure was low because of the low reactivity of the coke used. Carbons such as charcoal, of high reactivity, will give many fold this rate of CO₂ synthesis under conditions otherwise the same.

While the foregoing description and exemplary operations have served to illustrate specific applications and results of the invention, other modifications obvious to those skilled in the art are within the scope of the invention. Only such limitations should be imposed on the invention as are indicated in the appended claims.

What is claimed is:

1. A process for producing substantially pure CO₂ which comprises contacting a carbonaceous material in a reaction zone with finely divided solid copper oxide, maintaining the copper oxide in a uniform dense, turbulent fluidized state by means of CO₂ separately injected into the reaction zone, maintaining a temperature of 400 to 1000°C. In the reaction zone whereby reaction occurs between the carbonaceous material and the copper oxide to produce CO₂ and a reduced copper oxide, removing a gaseous stream of substantially pure CO₂ from the reaction zone, separating withdrawing a solids stream of reduced copper oxide from the reaction zone, reoxidizing the withdrawn reduced copper oxide in a separate oxidation zone by combustion with air, cooling the reoxidized copper oxide, purging the reoxidized copper oxide of air and gaseous combustion products by means of CO₂ gas and returning the reoxidized copper oxide to the reaction zone fluidized in CO₂.

2. A process according to claim 1 in which the carbonaceous material is a finely divided solid and in which the reaction temperature is maintained in the range of 800°C to 1000°C.

3. A process according to claim 1 in which the carbonaceous material is a gaseous hydrocarbon and in which the reaction temperature is maintained in the range of 600-800°C.

4. A process according to claim 1 in which the copper oxide is deposited on an inert solid carrier.

5. A process for the production of substantially pure CO₂ which comprises contacting finely divided coke in a reaction zone with finely divided solid copper oxide deposited on silica gel, maintaining the coke and oxide in a dense, turbulent, fluidized state in the reaction zone by means of CO₂ gas separately introduced thereto, maintaining a temperature of 800 to 1000°C. In the reaction zone whereby the coke is oxidized to CO₂ and the copper oxide is reduced, removing a gaseous stream of substantially pure CO₂ from the reaction zone, separately removing a solids stream of reduced copper oxide from the reaction zone, reoxidizing the reduced oxide in a separate oxidation zone by combustion with air, cooling the reoxidized copper oxide, purging the reoxidized copper oxide of air and gaseous combustion products by means of CO₂ gas, and returning the reoxidized copper oxide to the reaction zone fluidized in CO₂.

6. A process for the production of substantially pure CO₂ which comprises contacting methane in a reaction zone with finely divided solid copper oxide deposited on silica gel, maintaining the methane and oxide in a dense, turbulent, fluidized state in the reaction zone by means of CO₂ gas separately introduced thereto, maintaining a temperature of 400 to 800°C. In the reaction zone whereby the methane is oxidized to CO₂ and the copper oxide is reduced, removing a gaseous stream of substantially pure CO₂ from the reaction zone, separately removing a solids stream of reduced copper oxide from the reaction zone, reoxidizing the reduced oxide in a separate oxidation zone by combustion with air, cooling the reoxidized copper oxide, purging the reoxidized copper oxide of air and gaseous combustion products by means of CO₂ gas and returning the reoxidized copper oxide to the reaction zone fluidized in CO₂.

WARREN K. LEWIS,
EDWIN R. GILLILAND.

References Cited in the file of this patent

| FOREIGN PATENTS |
|------------------|-----------------|-----------|
| Number           | Country         | Date      |
| 936              | Great Britain   | 1862      |
| 16,789           | Great Britain   | 1897      |
| 12,156           | Great Britain   | 1993      |
| 6,835            | Great Britain   | 1896      |
| 587,774          | Great Britain   | May 6, 1947 |
| 597,231          | Great Britain   | Jan. 21, 1948 |

OTHER REFERENCES