

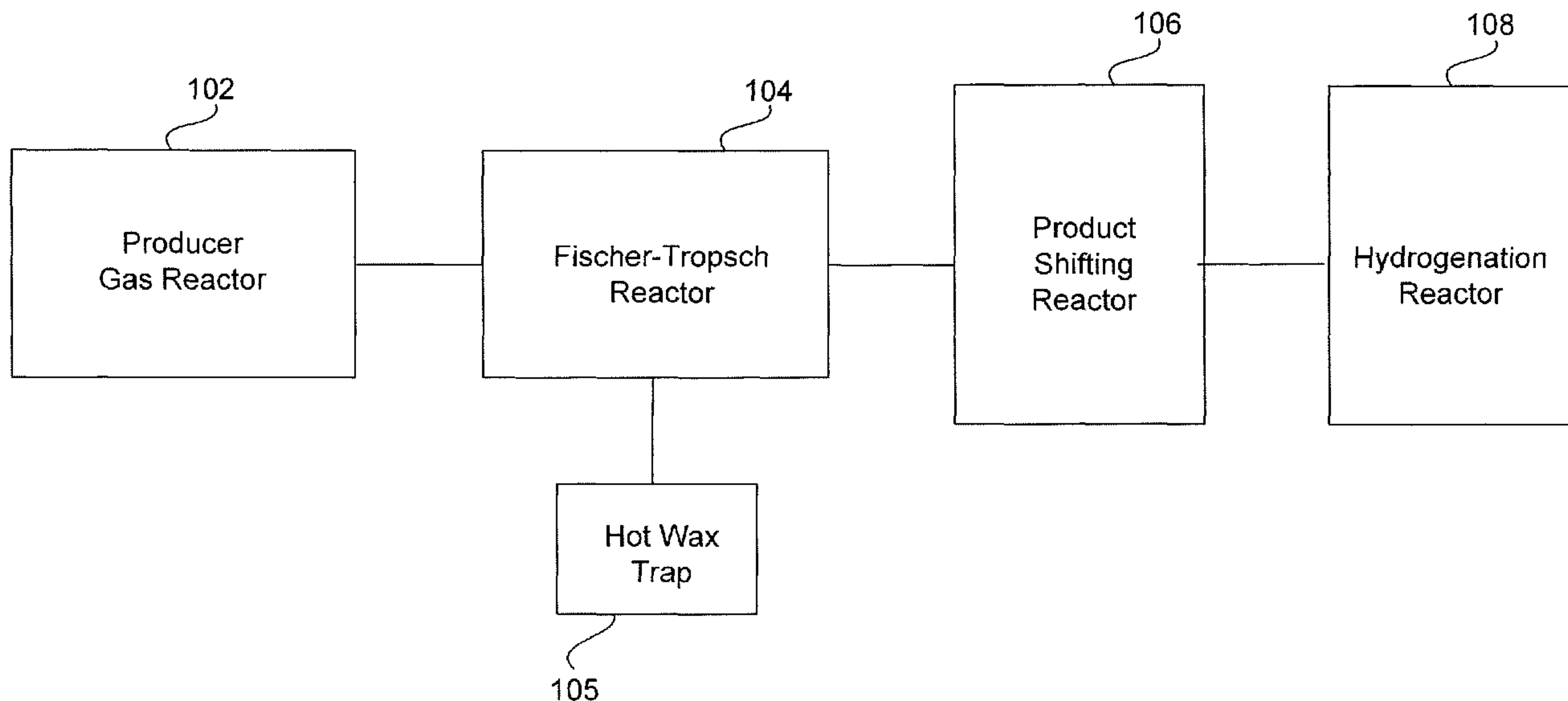


(86) Date de dépôt PCT/PCT Filing Date: 2009/08/06  
 (87) Date publication PCT/PCT Publication Date: 2010/02/11  
 (85) Entrée phase nationale/National Entry: 2011/02/08  
 (86) N° demande PCT/PCT Application No.: US 2009/052980  
 (87) N° publication PCT/PCT Publication No.: 2010/017372  
 (30) Priorités/Priorities: 2008/08/08 (US61/087,327);  
 2009/08/04 (US12/535,451)

(51) Cl.Int./Int.Cl. *C07C 27/00* (2006.01)  
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(54) Titre : CONVERSION DE CHARGES DE BIOMASSE EN CARBURANT DE TRANSPORT D'HYDROCARBURE LIQUIDE  
 (54) Title: CONVERSION OF BIOMASS FEEDSTOCKS INTO HYDROCARBON LIQUID TRANSPORTATION FUELS

**100**



**FIG. 1**

(57) **Abrégé/Abstract:**

Methods for converting a carbon-containing feedstock into liquid transportation fuels are described. The methods may include converting the carbon-containing feedstock into a producer gas made primarily of H<sub>2</sub>, CO, CO<sub>2</sub>, and N<sub>2</sub>, and reacting the producer

(57) **Abrégé(suite)/Abstract(continued):**

gas with a substrate catalyst to produce a combination of Fischer- Tropsch (FT) products, the FT products including the liquid transportation fuels. A portion of the FT products may be catalytically shifted to produce additional amounts of liquid transportation fuels. A portion of the FT products, or shifted FT products, may also be hydrogenated to produce additional amounts of stabilized liquid transportation fuels. Apparatuses are also described for employing one or more modular units to convert a carbon-containing feedstock into the liquid transportation fuels. The apparatuses may include a producer gas reactor, a Fischer-Tropsch reactor, a product-shifting reactor, and a hydrogenation reactor.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau(43) International Publication Date  
11 February 2010 (11.02.2010)(10) International Publication Number  
**WO 2010/017372 A1**(51) International Patent Classification:  
C07C 27/00 (2006.01)(21) International Application Number:  
PCT/US2009/052980(22) International Filing Date:  
6 August 2009 (06.08.2009)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
61/087,327 8 August 2008 (08.08.2008) US  
12/535,451 4 August 2009 (04.08.2009) US(71) Applicant (for all designated States except US): **COMMUNITY POWER CORPORATION** [US/US]; 8110 Shaffer Parkway, Suite 120, Littleton, CO 80127 (US).

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: CONVERSION OF BIOMASS FEEDSTOCKS INTO HYDROCARBON LIQUID TRANSPORTATION FUELS

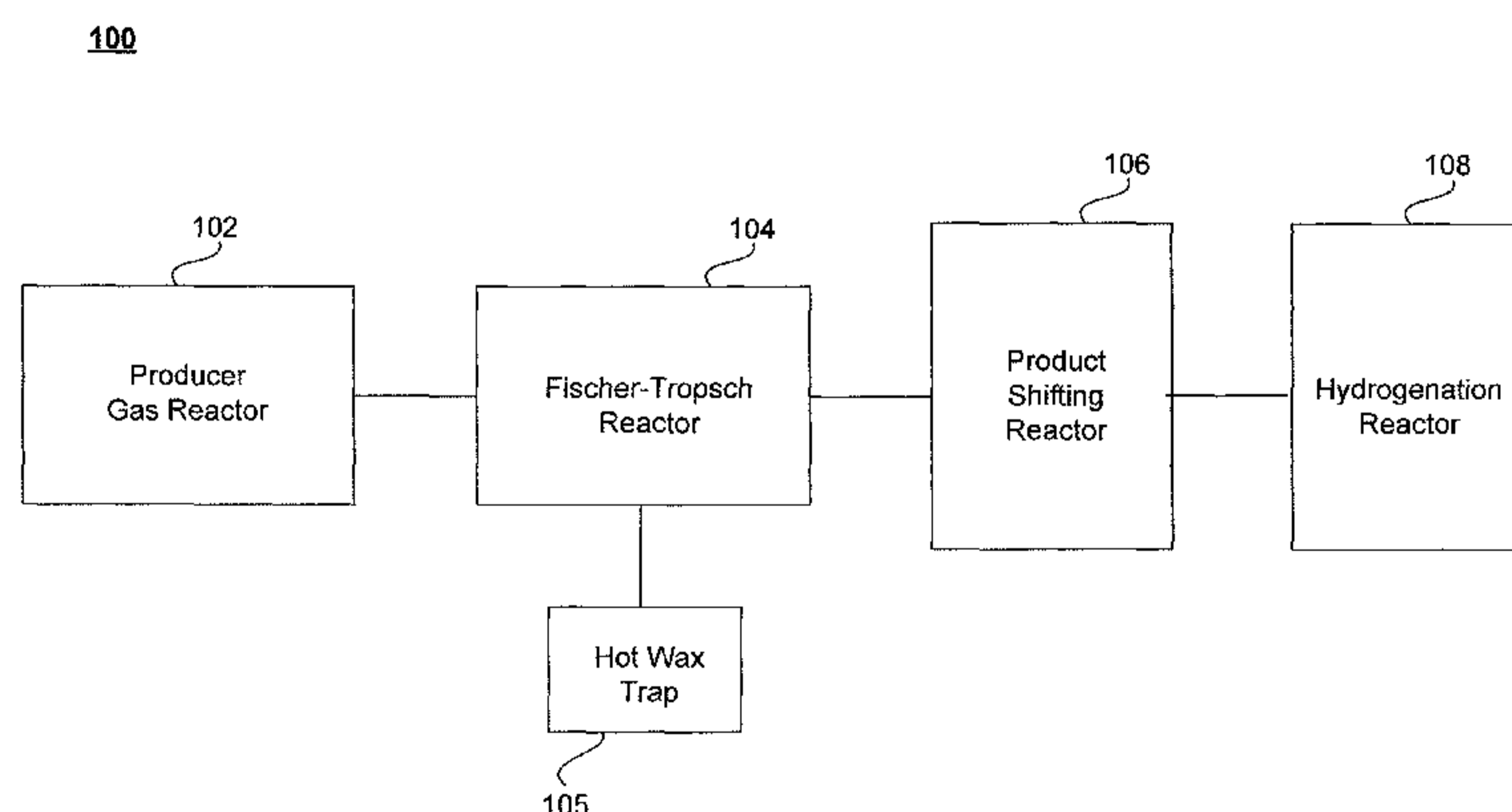


FIG. 1

(57) **Abstract:** Methods for converting a carbon-containing feedstock into liquid transportation fuels are described. The methods may include converting the carbon-containing feedstock into a producer gas made primarily of H<sub>2</sub>, CO, CO<sub>2</sub>, and N<sub>2</sub>, and reacting the producer gas with a substrate catalyst to produce a combination of Fischer-Tropsch (FT) products, the FT products including the liquid transportation fuels. A portion of the FT products may be catalytically shifted to produce additional amounts of liquid transportation fuels. A portion of the FT products, or shifted FT products, may also be hydrogenated to produce additional amounts of stabilized liquid transportation fuels. Apparatuses are also described for employing one or more modular units to convert a carbon-containing feedstock into the liquid transportation fuels. The apparatuses may include a producer gas reactor, a Fischer-Tropsch reactor, a product-shifting reactor, and a hydrogenation reactor.



WO 2010/017372 A1

## CONVERSION OF BIOMASS FEEDSTOCKS INTO HYDROCARBON LIQUID TRANSPORTATION FUELS

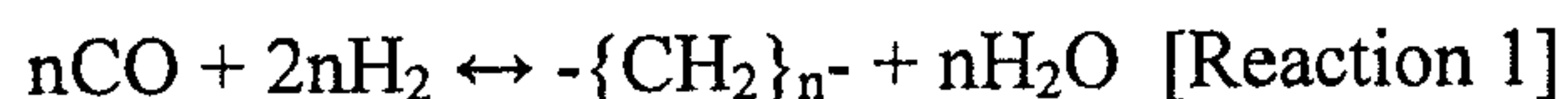
### CROSS-REFERENCES TO RELATED APPLICATIONS

5 [0001] This application claims the benefit of U.S. Provisional Application No. 61/087,327, filed August 8, 2008, the entire contents of which is herein incorporated by reference for all purposes.

### BACKGROUND OF THE INVENTION

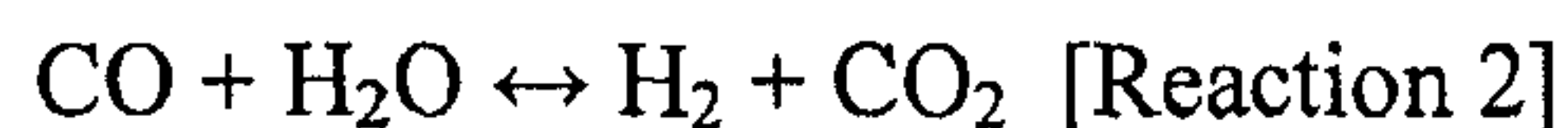
10 [0002] Commercial Gas-to-Liquid (GTL) systems for converting natural gas to into hydrocarbon liquid transportation fuels are often based on a multiplicity of complex refinery-based operations using oxygen-blown conversion of natural gas (or other fossil fuel-based resources) into synthesis gas (a.k.a. syngas) containing hydrogen (H<sub>2</sub>) and carbon monoxide (CO).

15 [0003] The perceived need to use oxygen, rather than air, to convert the carbon containing feedstock into syngas increases the capital and operating cost of the process considerably. Using air to gasify carbon-containing feedstocks to a mixture of CO and H<sub>2</sub> results in a large molecular nitrogen (N<sub>2</sub>) content. The mixture of CO, H<sub>2</sub>, CO, and N<sub>2</sub> is commonly called producer gas. It has been assumed that the high-N<sub>2</sub> content in producer gas interferes with  
20 the Fischer-Tropsch (FT) synthesis reactions. The syngas is converted into liquid hydrocarbon fuels and waxes through a series of Fischer-Tropsch synthesis reactions that are catalytically activated by a transition-metal based catalyst. The main FT synthesis reaction is the conversion of hydrogen and carbon monoxide into the liquid hydrocarbon fuel and water:



25 [0004] As Reaction 1 shows, each molecule of CO requires two molecules of H<sub>2</sub> to produce hydrocarbon products (liquid fuels and waxes) and one molecule of water (H<sub>2</sub>O). In Biomass to Liquid (BTL) systems, the gasification of biomass to produce a hydrogen-deficient syngas (containing an approximately 1:1 mole ratio of CO:H<sub>2</sub>) cannot sustain Reaction 1. Thus, for BTL systems, the CO:H<sub>2</sub> ratio may be adjusted through the Water-Gas-Shift (WGS) reaction

to convert a portion of the water vapor and CO in the gasified biomass to additional H<sub>2</sub> with CO<sub>2</sub> as a byproduct:



5 [0005] In many BTL systems, the WGS reaction is catalyzed by an iron-based Fischer-Tropsch catalyst so that approximately one-half the CO in the gas reacts with an equal molar amount of water vapor (which may be sourced from the Reaction 1) to produce H<sub>2</sub> and CO. The remaining CO is converted to FT synthesis products.

10 [0006] In most large-scale GTL and BTL systems, highly-purified syngas (containing primarily CO and H<sub>2</sub> with some CO<sub>2</sub>, but less than about 5% N<sub>2</sub>) is converted to heavy paraffinic FT synthesis waxes at pressure of 250 to 400 psig. In a series of refinery-based operations, the FT synthesis wax products are then cracked into gasoline and diesel-fuel products and hydrogenated to stabilize them during storage. Commercial GTL facilities are usually very large (typically producing several thousands of barrels per day of gasoline and diesel product) and have on-site oxygen and hydrogen generation plants to support the  
15 gasification and fuel upgrading systems.

[0007] Unfortunately, large-scale GTL and BTL systems require significant investments of capital to build. They also need to receive the proper approvals from regulatory, environmental, and zoning authorities that can limit the ability to build these systems near the biomass sources they will utilize to make the FT fuels. The systems also need to be coupled  
20 to or located near fuel transportation infrastructure to deliver the FT fuels to their final destination (e.g., gas stations). Given the large investment of capital and difficult source-to-end use logistics that are typical for these large scale systems, there is a need for new simpler methods and systems to generate FT fuels in an smaller, more distributed fashion.

## 25 BRIEF SUMMARY OF THE INVENTION

[0008] The conventional wisdom is that a small biorefinery would have poor economics. However, a small-scale biorefinery allows the use of low, or even negative cost feedstocks near their source, thereby reducing or even eliminating transportation of the feedstock and products, as well as, most distribution costs of the products. This small-scale paradigm, in  
30 conjunction with a greatly simplified conversion process, will allow the quick establishment of small-scale biorefineries in locations where feedstocks are cheap and comparative fuels are expensive due to transportation costs or scarcity. A small, factory built modular biorefinery

could be installed and operating in very short time compared to a large scale, field erected biorefinery.

[0009] Small, modular liquid fuel generation and processing systems are described for generation of liquid FT fuels on-site. The processes and systems may include the generation of producer gas made from biomass gasified in air that may be converted to FT liquid fuels. An advantage of this process is the discovery that air (rather than expensive pure oxygen) can be used to produce the gases used in the FT synthesis, greatly reducing the cost and complexity of the process. The processes and systems may also include refining the initial FT products into liquid fuel products such as gasoline, diesel, and/or aviation fuel. These small-scale processes and systems are a small fraction of the size and cost of conventional commercial GTL and BTL systems.

[0010] Embodiments of the invention include methods for converting a carbon-containing feedstock into a liquid transportation fuel. The methods may include converting the carbon-containing feedstock into a producer gas comprising primarily H<sub>2</sub>, CO, CO<sub>2</sub>, and N<sub>2</sub>, and reacting the producer gas with a substrate catalyst to produce a combination of Fischer-Tropsch (FT) products, where the FT products include liquid transportation fuels. The methods may also include the step of catalytically shifting portions of the undesirable FT products to produce additional amounts of the desired liquid transportation fuel. In addition, the methods may include hydrogenating a portion of the FT products to produce additional amounts of stabilized liquid transportation fuels.

[0011] Embodiments of the invention also include apparatuses for converting a carbon-containing feedstock into a liquid transportation fuel. The apparatuses may include a producer gas reactor operable to convert the carbon-containing feedstock into a producer gas comprising primarily H<sub>2</sub>, CO, CO<sub>2</sub>, and N<sub>2</sub>. The apparatuses may also include a Fischer-Tropsch reactor fluidly coupled to the producer gas reactor, where the Fischer-Tropsch reactor is operable to convert a portion of the producer gas on a simple, once-through basis into a combination of FT products, and where the FT products including the liquid transportation fuels. The apparatuses may also include a product-shifting reactor fluidly coupled to the Fischer-Tropsch reactor, where the product-shifting reactor is operable to catalytically convert portions of the FT products to produce additional amounts of the desired liquid transportation fuels. In addition the apparatuses may include a hydrogenation reactor fluidly coupled to the product-shifting reactor, where the hydrogenation reactor is operable to

hydrogenate a portion of the FT products to produce additional amounts of the stabilized liquid transportation fuels using hydrogen that may at least in part be sourced from the residual hydrogen in the byproduct gases.

5 [0012] Additional embodiments and features are set forth in part in the description that follows, and in part will become apparent to those skilled in the art upon examination of the specification or may be learned by the practice of the invention. The features and advantages of the invention may be realized and attained by means of the instrumentalities, combinations, and methods described in the specification.

10

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0013] A further understanding of the nature and advantages of the present invention may be realized by reference to the remaining portions of the specification and the drawings wherein like reference numerals are used throughout the several drawings to refer to similar components. In some instances, a sublabel is associated with a reference numeral and  
15 follows a hyphen to denote one of multiple similar components. When reference is made to a reference numeral without specification to an existing sublabel, it is intended to refer to all such multiple similar components.

[0014] Fig. 1 is a simplified schematic showing selected components of an apparatus for converting carbon-containing feedstocks to liquid transportation fuels according to  
20 embodiments of the invention;

[0015] Fig. 2 is a flowchart showing selected steps in a method of converting carbon-containing feedstocks to liquid transportation fuels according to embodiments of the invention;

[0016] Figs. 3A & B show simplified schematics of single and multiply coupled apparatus  
25 modules according to embodiments of the invention;

[0017] Figs. 4A-E show examples of cross-sectional geometries of FT reactor conduits according to embodiments of the invention;

[0018] Figs. 5A & B show examples of bundled arrangements of multiple FT reactor conduits according to embodiments of the invention; and

[0019] Fig 6 shows an example of a cross-sectional FT reactor conduit that also holds cooling conduits according to embodiments of the invention.

#### DETAILED DESCRIPTION OF THE INVENTION

5 [0020] Methods and systems are described for converting carbon-containing feedstocks to liquid transportation fuels such as gasoline, diesel, and aviation fuel, among other transportation fuels. The carbon-containing feedstocks may include biomass (*e.g.*, woodchips) that is gasified in the presence of air to make a producer gas that includes primarily hydrogen (H<sub>2</sub>), carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), and nitrogen (N<sub>2</sub>).  
10 The nitrogen is largely supplied by the air, and may account for about half of the volume of the producer gas.

[0021] The producer gas may be sent directly to a Fischer-Tropsch reactor without first to eliminating the molecular nitrogen (N<sub>2</sub>). It has been surprisingly discovered that the N<sub>2</sub> in the producer gas does not interfere with the functioning of the Fischer-Tropsch catalyst, and can  
15 even stabilize the production rates of the FT products by acting as a temperature moderating heat sink. The heat capacity of the N<sub>2</sub> can also allow larger diameter FT reactors (*e.g.*, about 2 to about 3½ inches in diameter versus about 1 inch for convention FT reactors) without runaway temperatures.

[0022] The Fischer-Tropsch catalyst may also be selected or treated to catalyze an *in-situ*  
20 water-gas-shift (WGS) reaction in the producer gas. Nitrogen-diluted producer gas made from biomass feedstocks typically has a CO:H<sub>2</sub> ratio of about 1:0.7, while the ratio should be closer to about 1:2 to sustain the production of FT products. When the Fischer-Tropsch catalyst can catalyze the WGS reaction, the adjustment of the CO:H<sub>2</sub> ratio can take place efficiently at the FT catalyzation site instead of in a physically separated WGS reactor.

25 [0023] The present individual apparatuses are significantly simpler than conventional Fischer-Tropsch systems, and may be simple enough for small portable operations that are co-located with a biomass feedstock source (*e.g.*, wooded area) and/or a transportation fuel depot such as a garage, gas-station, marina, airport, *etc.* Single, standalone modular units like the single unit 300 shown in Fig. 3A may also be combined together to create a facility with  
30 much larger liquid fuel production capacity. Fig. 3B, for example, shows a arrangement of six individual units 302a-f arranged in a 2x3 array. The individual units 302a-f are coupled

together to convert carbon-containing feedstock into the liquid transportation fuel and other FT products in higher quantities and/or faster rates than single unit 300.

[0024] It will be appreciated that array of units 302a-f show in Fig. 3B is but one of many ways that multiple units can be coupled together. The modular nature of the units permit flexibility in the scaling of multiple coupled units. For example, a single unit may be coupled to one or more additional modular units, as required by an operation's fuel production requirements. Individual units may also be added or removed from the array as fuel product needs change over time. This flexible process can significantly reduce construction costs and time, fuel production costs, and the energy needed to transport the carbon feedstock to the apparatus and the liquid fuel to end-use transportation vehicle, among other costs. Further details of embodiments of the present apparatuses and methods are given below.

#### Exemplary Apparatuses

[0025] Fig. 1 shows a simplified schematic of selected components of an apparatus 100 for converting carbon-containing feedstocks to liquid transportation fuels according to embodiments of the invention. The apparatus 100 may include a producer gas reactor 102 that mixes a carbon-containing feedstock with air to make a producer gas. The feedstock may include gaseous, liquid or solid hydrocarbons. Examples of these hydrocarbons include coal, peat, plastics, heavy oil, light olefin hydrocarbons, natural gas, methane, ethane and/or other gaseous or liquid alkanes, alkenes, or alkynes.

[0026] The producer gas reactor 102 may also be a gasification reactor that converts carbon-containing biomass and air into producer gas. This biomass may include woody biomass, non-woody biomass, cellulosic products, cardboard, fiber board, paper, plastic, and food stuffs among other biomass. Biomass may also include human refuse that can have a negative cost as the refuse suppliers actually pay to have the refuse removed from a premises (e.g., a production facility, an office building, a restaurant, etc). Many types of biomass have low levels of sulfur and heavy metal contaminants compared to conventional hydrocarbon fuel sources like oil and coal. The moisture content of the biomass may be adjusted to about 5 wt.% to about 35 wt.%, (e.g., about 5 wt.% to about 20 wt.%) and placed in the gasification reactor where it is heated in the presence of air to form the producer gas.

[0027] When the feedstock is biomass, the producer gas may be a product of the partial combustion of the biomass with molecular oxygen (O<sub>2</sub>) from the supplied air. This is a controlled partial combustion process designed to partially oxidize the largest portion of the

biomass into H<sub>2</sub> and CO instead of fully oxidized H<sub>2</sub>O and CO<sub>2</sub> (although both these gases are present in the producer gas). An example of a modular biomass gasification reactor that may be incorporated into embodiments of the apparatus is described in U.S. Pat. App. Ser. No. 11/427,231, filed June 28, 2006 and titled "Method And Apparatus For Automated, Modular, Biomass Power Generation", the entire contents of which are herein incorporated by reference for all purposes.

**[0028]** The molecular nitrogen (N<sub>2</sub>) in the air is relatively unreactive with the carbon-containing feedstock, and mostly remains unchanged in the producer gas. Air is about 79 vol. % N<sub>2</sub>, and the N<sub>2</sub> may account for about 40 to 50 vol.% of the producer gas. Typically, conventional FT GTL and BTL systems remove most or all of the N<sub>2</sub> in the air using an air separation unit (ASU) and only send purified oxygen to the gasifier 102 to make a low-nitrogen containing syngas to send to the FT reactor 104. However, it has been surprisingly discovered that separating the N<sub>2</sub> from the air used in gasification is not necessary, and that the producer gas, diluted with nitrogen from the air, may be sent directly to the FT reactor 104 and successfully be used to make FT products.

**[0029]** The FT reactor 104 may include a substrate catalyst to convert CO and H<sub>2</sub> into FT products as shown in Reaction 1 above. The substrate catalyst may be a transition metal and/or transition metal oxide based material such as iron and/or an iron oxide. Examples of iron-containing minerals used in the catalyst substrate including, but not limited to, magnetite and hematite, among other minerals. The substrate catalyst may also be selected and/or treated so that it will also catalyze an in-situ water-gas-shift (WGS) reaction (see Reaction 2) to tip the ratio of CO:H<sub>2</sub> towards 1:2. For example, when the substrate catalyst is an iron-containing catalyst, it may be treated with a copper or potassium promoter that also makes it a WGS reaction catalyst. The substrate catalyst may also be exposed to a reducing atmosphere to activate FT reaction sites on the substrate catalyst.

**[0030]** As noted above, when the nitrogen (N<sub>2</sub>) is left in the producer gas its heat capacity may allow larger amounts of the FT substrate catalyst to be packed into the FT reactor 104. Figs. 4A-E show examples of cross-sectional geometries of FT reactor conduits for holding the FT substrate catalyst according to embodiments of the invention. Fig 4A shows a circular conduit geometry that may be seen where the substrate catalyst is held by a cylindrically-shaped tube about 2 to about 3½ inches in diameter compared to about 1 inch for conventional BTL systems. Figs. 4B-E show conduit geometries where the holder for the

substrate catalyst have a non-circular shapes, such as square (Fig. 4B), elliptical (Fig. 4C), triangular (Fig. 4D), trapezoidal (Fig. 4E), and hexagonal (Fig. 4F). It will be appreciated that additional shapes (*e.g.*, polygonal, hemispherical, *etc.*) may also be used. The producer gas may flow through the conduit at a temperature of about 250 °C to about 300 °C. The nitrogen may also allow the FT reactor 104 to operate at lower pressure of about 250 psig or less (*e.g.*, 150 psig) compared to conventional BTL systems which operate closer to about 300 psig.

[0031] It should also be appreciated that a plurality of conduits may be bundled into a multi-conduit array in the FT reactor 104. Fig. 5A, for example, shows a hexagonal arrangement 502 of a plurality of conduits 504, each having a circular cross-sectional shape. In additional embodiments (not shown) the individual conduits may comprise two or more different cross-sectional shapes, and may have a different geometric arrangement (*e.g.*, square, triangular, circular, elliptical, *etc.*). The scalability of the conduit bundles is exemplified in Fig. 5B, which shows a hexagonal arrangement 506 of seven arrays 502 of individual conduits 504. Figs. 5A & B illustrate the scalability of the FT reactor 104, similar to the scalability of whole modular units as shown in Figs. 3A & B.

[0032] It should be further appreciated that the FT reactor 104 may include a conduit that holds cooling structures that are thermally coupled to the FT substrate catalyst in the conduit. Fig. 6 shows an example of a conduit 602 that holds three inner cooling tubes 606a-c in addition to the FT catalyst substrate 604. The cooling tubes 606a-c may contain a flowing stream of coolant 608 that absorbs heat from the surrounding FT catalyst substrate 604 and transports it from the conduit 602. The coolant may be any coolant fluid (*i.e.*, liquid or gas) compatible with the cooling tubes 606a-c and capable of absorbing heat energy at rates that can stabilize the temperature of the FT catalyst substrate 604 during operation of the reactor.

[0033] The FT products generated by the FT reactor 104 may include the liquid transportation fuels such as gasoline, synthetic paraffinic kerosene (SPK), diesel fuel, and aviation fuel. The FT products may also include smaller hydrocarbons such as methane, ethane, propanes, butanes, light olefins (*e.g.*, ethylene, propylene and butelenes), *etc.*, as well as larger hydrocarbons such as paraffinic waxes. These smaller and larger products may be converted into additional liquid transportation fuels by the product-shifting reactor 106 and the hydrogenation reactor 108.

[0034] A hot wax trap 105 may be optionally coupled to the FT reactor 104. This trap captures hydrocarbon waxes that make up part of the FT products. The trap 105 may be configured for the recovery of the waxes, which are also useful FT products.

5 [0035] The product-shifting reactor 106 may catalytically crack the larger hydrocarbons (e.g., waxes) into liquid transportation fuels and may also condense unsaturated carbon-carbon bonds in, for example, light olefins to make alkyl substituted aromatic liquid transportation fuels. The cracking process may reduce the amount of larger, waxy hydrocarbon FT products from about 20 wt.% to less than 5 wt.%.

10 [0036] The product-shifting reactor 106 may include a cracking catalyst, such as a ZSM-5 synthetic zeolite (e.g., H-ZSM-5). These zeolites are available commercially as a generic commodity product. For example, a suitable zeolite used in embodiments of the present product-shifting reactor 106 include H-ZSM-5 from Zeolyst International.

15 [0037] Some of the FT products generated by the FT reactor 104, as well as some of the cracked hydrocarbon products generated by the product-shifting reactor 106 may be hydrogenated in hydrogenation reactor 108 to produce additional liquid transportation fuels. The hydrogenation reactor 108 includes a hydrogenation catalyst that catalyzes the reaction of residual molecular hydrogen (H<sub>2</sub>) in the byproduct gas with unsaturated carbon-carbon bonds in the shifted and/or unshifted FT products to produce unsaturated liquid transport fuels. When the FT catalyst in the FT reactor 104 is also catalyzing a WGS reaction, enough  
20 molecular hydrogen may be present in the byproduct gas so that no additional outside source of hydrogen is needed for the hydrogenation reactor 108.

[0038] The hydrogenation catalyst may include a palladium or platinum containing catalyst, such as 0.5% palladium on alumina. This material is commercially available from Aldrich Chemical Company (Aldrich No. 520675).

## 25 Exemplary Methods

[0039] Fig. 2 shows a flowchart with selected steps in a method 200 of converting carbon-containing feedstocks to liquid transportation fuels according to embodiments of the invention. The method 200 may include the step of converting a carbon-containing feedstock into a producer gas (202). When the feedstock is a simple alkane such as methane, a partial  
30 oxidation of the methane with air produces a syngas (*i.e.*, H<sub>2</sub> + CO) diluted in molecular nitrogen, which is the producer gas. Because the C:H ratio in methane is higher than other

carbon-feedstocks like biomass, the CO:H<sub>2</sub> ratio is also higher, and may already be at the 1:2 ratio necessary for a sustained FT reaction step (see Reaction 1).

[0040] When feedstocks like biomass are gasified into producer gas, the ratio CO:H<sub>2</sub> is about 1:0.7 and should be adjusted (204) closer to 1:2. This adjustment in the ratio may be done by a water-gas-shift (WGS) reaction in the same location as the producer gas is generated, in-situ at the site of the Fischer-Tropsch reaction, in a separate WGS reactor, or a combination of these locations.

[0041] Once the producer gas has about a 1:2 ratio of CO:H<sub>2</sub>, either initially or with the help of a WGS reaction, at least a portion of the producer gas may be converted to FT products (206) through a catalytic FT reaction. As noted above, some of the FT products are liquid transportation fuels that need no additional conversions or treatments. Other FT products are molecules that are either too small or too large to be liquid transportation fuels, and a portion of these products may be further converted into additional transportation fuels.

[0042] These further conversion processes may include catalytically cracking the FT products (208). Large, waxy FT products may be cracked into smaller liquid transportation fuels, and smaller FT products may be combined to form olefinic and alkyl substituted aromatic components of transportation fuels. Three moles of hydrogen are released during the formation of one mole of aromatic compounds, which are available to hydrogenate and saturate the olefinic products. The conversion processes may also include hydrogenating some of the FT products (210). These may include direct products from the FT reaction, as well as catalytically shifted products that still have one or more unsaturated bonds.

[0043] The liquid transportation fuels produced by the apparatuses and methods may include room temperature liquids and gases used in transportation vehicles, including cars, trucks, boats, and airplanes, among other vehicles. The initial mixture of the liquid transportation fuels emerging from the present apparatuses may be separated into refined transportation fuels by conventional distillation and refining techniques. Because the fuels are relatively low in sulfur and other contaminants, less scrubber/purifying equipment is needed to make the final transportation fuel.

[0044] Embodiments may also include methods for converting the carbon-containing feedstock into predominantly hydrocarbon waxes instead of liquid transportation fuels. These embodiments may include bypassing the catalytic cracking and hydrogenation of the FT products and instead recycling them through the site of the FT reaction one or more times.

The additional exposure of the FT products to a FT catalyst causes additional combination of smaller products into larger ones, including the hydrocarbon waxes. The heavy liquid and solid waxes may be recovered from a hot wax trap of the apparatus.

### Exemplary Systems

5 [0045] Exemplary systems have been demonstrated to operate with compressed producer gas from the gasification of biomass. These systems were able to repeatedly shut down, temperature cycle, and restart the production of liquid FT transport fuels with little or no loss of catalytic activity. Subsequent separation of the FT products into high-octane syngasoline and high-cetane syndiesel fractions is easily accomplished by a simple distillation step.

### 10 Exemplary Fischer-Tropsch Reactor Systems

[0046] Embodiments of the FT Reactor System may include a fixed-bed producer gas-to-liquid system that operates at relatively low pressures (*e.g.*, about 170 psig to about 240 psig) to make the FT process more amenable to small, distributed modular applications. The FT catalyst used in the system may be based on an inexpensive iron mineral-based particulate  
15 substrate capable of catalyzing *in-situ* water-gas-shift reactions, as well as FT synthesis reactions. This way, the gasified biomass is not required to pass through a separate WGS reactor to adjust the mole ratio of CO:H<sub>2</sub> closer to 1:2.

[0047] The preparation of the substrate catalyst may include mixing the substrate with a blend of inorganic salt solutions to adjust the relative rate of the WGS reaction compared  
20 with the FTS reaction. The inorganic salts may also be selected to influence the quantities and types of FT products that are produced. Preparation may also include reducing the substrate with hydrogen to activate catalytic sites on the substrate's surface. In addition, a catalytically-active form of carbon may be deposited on the reduced substrate.

[0048] The substrate catalyst can take advantage of the large amount of N<sub>2</sub> in producer gas  
25 to increase reaction rates and yields of liquid FT transportation fuels at higher temperatures. In contrast, conventional FT catalysts are designed to work with pure syngas that contains primarily CO and H<sub>2</sub> without the N<sub>2</sub> present. The substrate catalyst can convert the producer gas into a variety of FT products, including methane, ethane, propanes, butanes, light olefins (*e.g.*, ethylene, propylene, butelenes, *etc.*), gasoline, synthetic paraffinic kerosene (SPK),  
30 diesel fuels, and waxes, among other products. Some of these products, such as the waxes and light olefins, may be converted into additional stable liquid fuels by cracking,

polymerization, and/or alkylation coupled with hydrogenation. Embodiments of present reactor systems may include downstream reactors for product-shifting and/or hydrogenation.

#### Exemplary Product-Shifting Reactor

[0049] In a downstream processing step, raw FT products may be sent through a packed  
5 bed of a zeolite cracking catalyst to convert high molecular weight waxes to room-  
temperature liquid fuels, and to condense light olefins to methyl and ethyl substituted  
aromatic gasoline and diesel constituents. The zeolite may be an H-ZSM-5 catalyst from  
Zeolyst International for cracking waxes and aromatizing light olefins. The multipurpose  
ZSM-5 zeolites were originally developed by Mobil Oil Company in the 1970s to crack  
10 heavy oils, polymerize olefins, alkylate aromatics, and convert methanol to aromatic gasoline  
constituents. In recent tests the H-ZSM-5 catalyst has demonstrated a reduction in waxy FT  
hydrocarbons from about 20 wt.% to about 5 wt.%

#### Exemplary Hydrogenation Reactor

[0050] In another downstream processing step, dewaxed liquid fuels from the product  
15 shifting operations may be sent through a fixed bed of palladium hydrogenation catalyst to  
saturate olefinic sites and thereby stabilize the liquid fuel products. A hydrogenation catalyst  
that contains about 0.5% palladium on alumina (e.g., Aldrich No. 520675) may be used in the  
hydrogenation reactor. Tests from current operations indicate the partial pressure of residual  
hydrogen in the process gas (around 12 vol. %) is sufficient to hydrogenate and stabilize  
20 reactive olefin sites.

#### Analysis of FT Product Distributions

[0051] GC/MS analysis of FT products (a.k.a. syngasoline) from an embodiment of the BTL  
system show branched hydrocarbons are the major constituents of the syngasoline fraction,  
along with some methyl- and ethyl- substituted monocyclic aromatics. The raw syngasoline  
25 fraction has a projected relatively high octane rating. Like most ultra-low sulfur FT liquid  
fuels, straight-chain hydrocarbons are the major constituents of CPC's synthetic diesel  
(syndiesel) product. Our syndiesel, however, also contains small amounts (e.g., less than 15  
wt. %) of methyl- and ethyl-monocyclic aromatics from the H-ZSM-5 product shifting  
operations. This results in a FT fuel with a desirable lower cloud point and fewer anticipated  
30 problems with elastomeric seals than more typical, highly paraffinic FT fuels.

#### Estimated Product Yields

**[0052]** A bench-top continuous-flow system has demonstrated over 75% conversion of CO in a two-stage simulation, with half the CO consumption for FT production of liquid fuels, and the other half used to generate more hydrogen and eliminate waste water via the WGS reaction. Assuming 70% of the hydrocarbon products are the gasoline and diesel fuel  
5 fractions, the projected yield of the system is around 42 gallons of synfuels per ton of dry biomass. This quantity of liquid hydrocarbon fuel contains the energy of about 68 gallons of ethanol.

**[0053]** The CO consumption by the WGS reaction may be reduced by employing a hydrogen-selective membrane to recover and recycle hydrogen from the system off-gas,  
10 which increases the projected yields of liquid fuels by 15% to a projected 48 gallons of hydrocarbons/ton of dry biomass (equivalent to 78 gallons of ethanol per ton). Product separation is by gas/liquid disengagement methods and distillation of the liquids. The byproduct gases from this single-pass process contain residual hydrogen, carbon monoxide, methane, ethane, propane, butanes, etc. This byproduct mixture is combustible and can be  
15 burned in a boiler to produce steam or to fuel an internal or external combustion engine to produce process heat and electricity to power the overall process.

**[0054]** Having described several embodiments, it will be recognized by those of skill in the art that various modifications, alternative constructions, and equivalents may be used without departing from the spirit of the invention. Additionally, a number of well-known processes  
20 and elements have not been described in order to avoid unnecessarily obscuring the present invention. Accordingly, the above description should not be taken as limiting the scope of the invention.

**[0055]** Where a range of values is provided, it is understood that each intervening value, to the tenth of the unit of the lower limit unless the context clearly dictates otherwise, between  
25 the upper and lower limits of that range is also specifically disclosed. Each smaller range between any stated value or intervening value in a stated range and any other stated or intervening value in that stated range is encompassed. The upper and lower limits of these smaller ranges may independently be included or excluded in the range, and each range where either, neither or both limits are included in the smaller ranges is also encompassed  
30 within the invention, subject to any specifically excluded limit in the stated range. Where the stated range includes one or both of the limits, ranges excluding either or both of those included limits are also included.

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[0056] As used herein and in the appended claims, the singular forms "a", "an", and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "a process" includes a plurality of such processes and reference to "the catalyst" includes reference to one or more catalysts and equivalents thereof known to those skilled in the art, and so forth.

[0057] Also, the words "comprise," "comprising," "include," "including," and "includes" when used in this specification and in the following claims are intended to specify the presence of stated features, integers, components, or steps, but they do not preclude the presence or addition of one or more other features, integers, components, steps, acts, or groups.

WHAT IS CLAIMED IS:

- 1           1.       A method for converting a carbon-containing feedstock into liquid  
2 transportation fuels, the method comprising:  
3           converting the carbon-containing feedstock into a producer gas comprising H<sub>2</sub>,  
4 CO, CO<sub>2</sub>, and N<sub>2</sub>;  
5           reacting the producer gas with a substrate catalyst to produce a combination of  
6 Fischer-Tropsch (FT) products, the FT products including the liquid transportation fuels;  
7           catalytically shifting a portion of the FT products to produce additional  
8 amounts of the liquid transportation fuels; and  
9           hydrogenating a portion of the FT products to produce additional amounts of  
10 the liquid transportation fuels.
- 1           2.       The method of claim 1, wherein the carbon-containing feedstock  
2 comprises biomass.
- 1           3.       The method of claim 1, wherein the biomass has a water content from  
2 about 5 wt. % to about 35 wt. %.
- 1           4.       The method of claim 1, wherein the biomass has a water content from  
2 about 5 wt. % to about 20 wt. %.
- 1           5.       The method of claim 1, wherein the carbon-containing feedstock  
2 comprises methane, petroleum refinery byproducts, coal, or peat.
- 1           6.       The method of claim 1, wherein the liquid transportation fuels are  
2 selected from the group consisting of gasoline, diesel fuel, aviation fuel, and synthetic  
3 paraffinic kerosene.
- 1           7.       The method of claim 1, wherein the N<sub>2</sub> comprises about 30 vol. % to  
2 about 60 vol.% of the producer gas.
- 1           8.       The method of claim 1, wherein the method further comprises  
2 increasing the ratio of H<sub>2</sub>:CO by having a portion of the producer gas undergo a water-gas-  
3 shift (WGS) reaction.

- 1           9.       The method of claim 8, wherein the WGS reaction is catalyzed by the  
2 substrate catalyst.
- 1           10.       The method of claim 1, wherein the FT products are selected from the  
2 group consisting of methane, ethane, propanes, butanes, light olefins, gasoline, synthetic  
3 paraffinic kerosene, kerosene, aviation fuel, diesel fuel, fuel oils, and waxes.
- 1           11.       The method of claim 10, wherein the light olefins comprise ethylene,  
2 propylene, or butylenes.
- 1           12.       The method of claim 1, wherein the step of catalytically shifting a  
2 portion of the FT products comprises:  
3           contacting the FT products with a zeolite catalyst; and  
4           splitting an FT product constituent comprising a wax into two or more smaller  
5 hydrocarbons with the zeolite catalyst;  
6           aromatizing an FT product constituent comprising a light olefin into an alkyl-  
7 aromatic compound; and  
8           polymerizing light olefins to form larger olefinic compounds.
- 1           13.       The method of claim 12, wherein the alkyl-aromatic compound is  
2 selected from the group consisting of toluene, ethyl benzene, xylenes, ethyl toluene, propyl  
3 benzenes, propyl toluenes, butyl benzenes, ethyl propyl benzene, and butyl toluene.
- 1           14.       The method of claim 1, wherein the step of hydrogenating a portion of  
2 the FT products comprises hydrogenating unsaturated hydrocarbons produced by the catalytic  
3 shifting step.
- 1           15.       The method of claim 1, wherein the step of hydrogenating a portion of  
2 the FT products comprises flowing at least a portion of the FT products through a fixed bed  
3 of a hydrogenation catalyst comprising palladium, platinum, or a combination of palladium  
4 and platinum.
- 1           16.       The method of claim 15, wherein the palladium hydrogenation catalyst  
2 comprises about 0.5 wt% palladium on an alumina substrate.

1           17.     The method of claim 1, wherein the step of hydrogenating a portion of  
2 the FT products comprises exclusively or partially supplying hydrogen for the hydrogenation  
3 from the producer gas.

1           18.     The method of claim 1, wherein the step of hydrogenating a portion of  
2 the FT products comprises supplying hydrogen for the hydrogenation from byproduct gas or  
3 hydrogen recovered from waste byproduct gas.

1           19.     The method of claim 1, wherein the method further comprises cooling  
2 the substrate catalyst with the N<sub>2</sub> in the producer gas.

1           20.     The method of claim 1, wherein a pressure for reacting the producer  
2 gas with the substrate catalyst is about 250 psig or less.

1           21.     The method of claim 1, wherein a temperature for reacting the  
2 producer gas with the substrate is about 300 °C or less.

1           22.     The method of claim 1, wherein a temperature for reacting the  
2 producer gas with the substrate catalyst is about 250 °C to about 300 °C.

1           23.     An apparatus for converting a carbon-containing feedstock into a  
2 liquid transportation fuel, the apparatus comprising:  
3           a producer gas reactor operable to convert the carbon-containing feedstock  
4 into a producer gas comprising N<sub>2</sub>, CO, H<sub>2</sub>, and CO<sub>2</sub>; and  
5           a Fischer-Tropsch reactor fluidly coupled to the producer gas reactor, wherein  
6 the Fischer-Tropsch reactor is operable to convert a portion of the producer gas into a  
7 combination of Fischer-Tropsch (FT) products, the FT products including the liquid  
8 transportation fuel;  
9           a shifting reactor fluidly coupled to the Fischer-Tropsch reactor, wherein the  
10 shifting reactor is operable to catalytically convert a portion of the FT products to produce  
11 additional amounts of the liquid transportation fuel; and  
12           a hydrogenation reactor fluidly coupled to the cracking reactor, wherein the  
13 hydrogenation reactor is operable to hydrogenate a portion of the FT products to produce  
14 additional amounts of the liquid transportation fuel.

1           24.     The apparatus of claim 23, wherein the producer gas reactor is a  
2 biomass gasification reactor operable to convert biomass and air into the producer gas.

1           25.     The apparatus of claim 24, wherein the biomass is selected from the  
2 group consisting of woody biomass, non-woody biomass, a cellulosic product, a lignin  
3 product or byproduct, cardboard, fiber board, paper, plastic, and a food stuff.

1           26.     The apparatus of claim 23, wherein the Fischer-Tropsch reactor  
2 comprises a conduit filled with a Fischer-Tropsch catalyst, wherein the conduit has an inner  
3 cross-sectional area ranging from about 3 square inches to about 10 square inches.

1           27.     The apparatus of claim 26, wherein the conduit has a cross-sectional  
2 shape selected from the group consisting of circular, elliptical, triangular, square, rectangular,  
3 trapezoidal, polygonal.

1           28.     The apparatus of claim 26, wherein the conduit comprises a cylindrical  
2 tube having a diameter ranging from about 2 inches to about 3.5 inches.

1           29.     The apparatus of claim 23, wherein the the Fischer-Tropsch reactor  
2 comprises a plurality of conduits, each filed with a Fischer-Tropsch catalyst.

1           30.     The apparatus of claim 23, wherein the Fischer-Tropsch reactor  
2 comprises a Fischer-Tropsch catalyst comprising iron.

1           31.     The apparatus of claim 23, wherein the Fischer-Tropsch reactor  
2 comprises a Fischer-Tropsch catalyst operable to catalyze a water-gas-shift reaction between  
3 H<sub>2</sub>O and CO to produce H<sub>2</sub> and CO<sub>2</sub>.

1           32.     The apparatus of claim 23, wherein the shifting reactor comprises a  
2 zeolite catalyst that can catalytically crack waxes, aromatize light olefins, and polymerize  
3 light olefins.

1           33.     The apparatus of claim 32, wherein the zeolite comprises a ZSM-5  
2 zeolite.

1           34.     The apparatus of claim 23, wherein the hydrogenation reactor  
2 comprises a hydrogenation catalyst comprising palladium.

1           35.     The apparatus of claim 34, wherein the hydrogenation catalyst  
2 comprises palladium on alumina.

1           36.     The apparatus of claim 23, wherein the apparatus is a single module  
2 that may be coupled with one or more additional modules to make a scaled apparatus that  
3 converts the carbon-containing feedstock into the liquid transportation fuel at a faster rate  
4 than the single module.

1           37.     A method for converting a carbon-containing feedstock into  
2 hydrocarbon waxes, the method comprising:  
3           converting the carbon-containing feedstock into a producer gas comprising H<sub>2</sub>,  
4 CO, CO<sub>2</sub>, and N<sub>2</sub>;  
5           reacting the producer gas with a substrate catalyst to produce a combination of  
6 Fischer-Tropsch (FT) products, the FT products including hydrocarbon gases and liquids, and  
7 a first portion of the hydrocarbon waxes; and  
8           reacting at least a portion of the hydrocarbon gases and liquids with the  
9 substrate catalyst to produce a second portion of the hydrocarbon waxes.

100

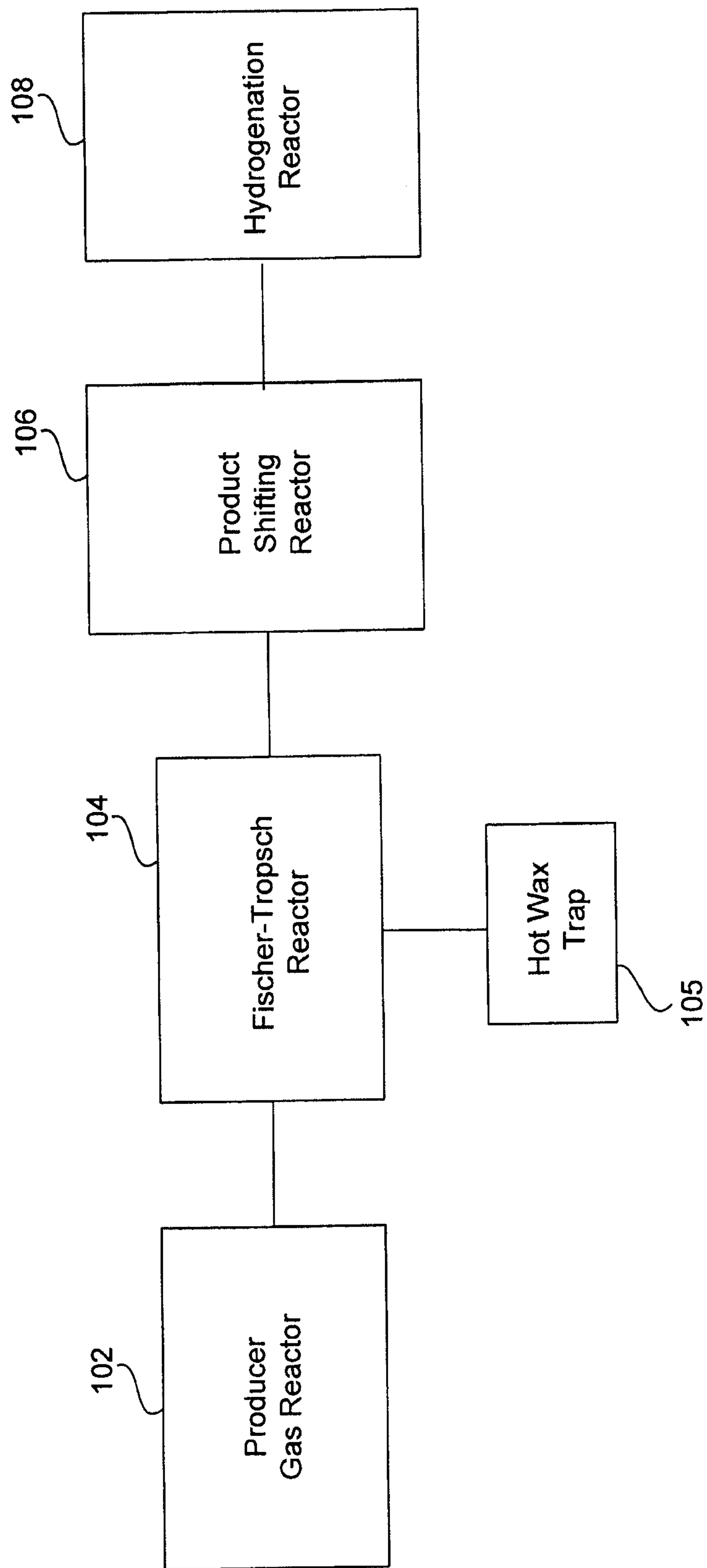


FIG. 1

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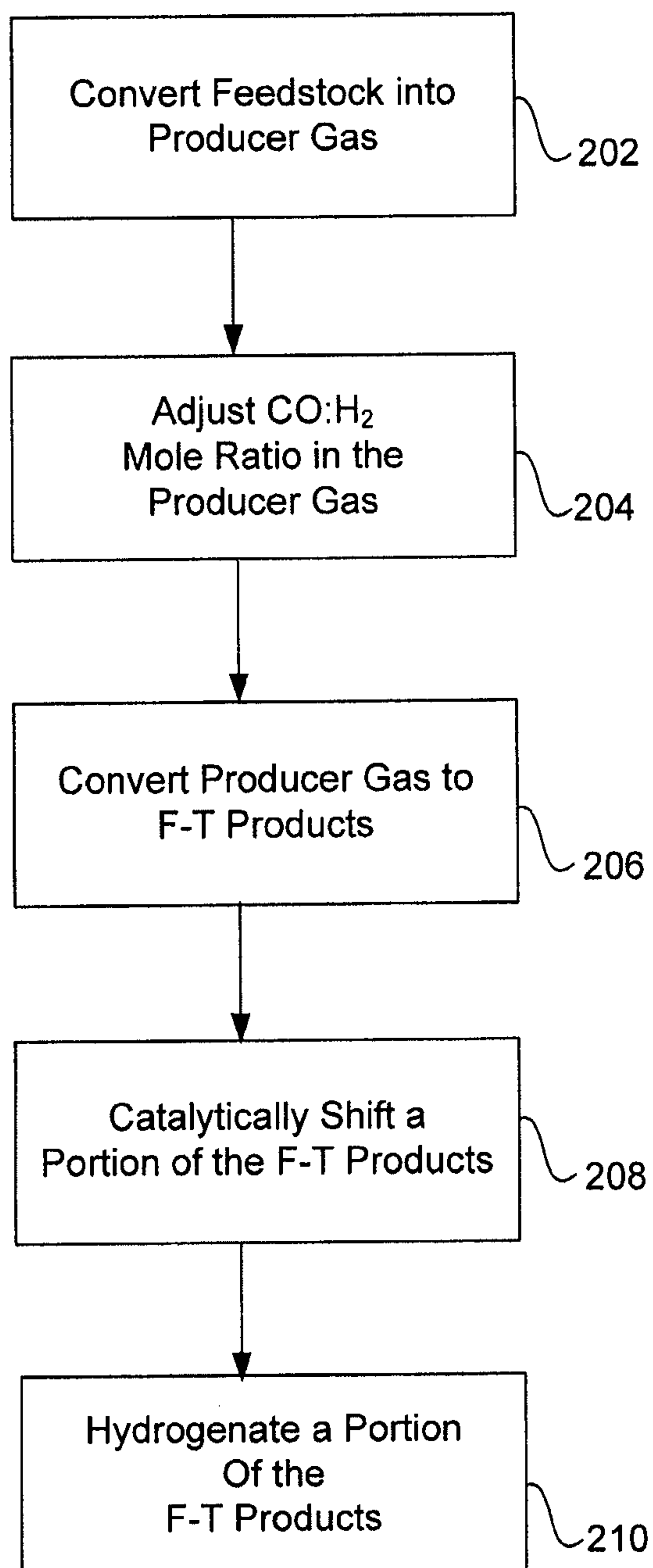
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FIG. 2

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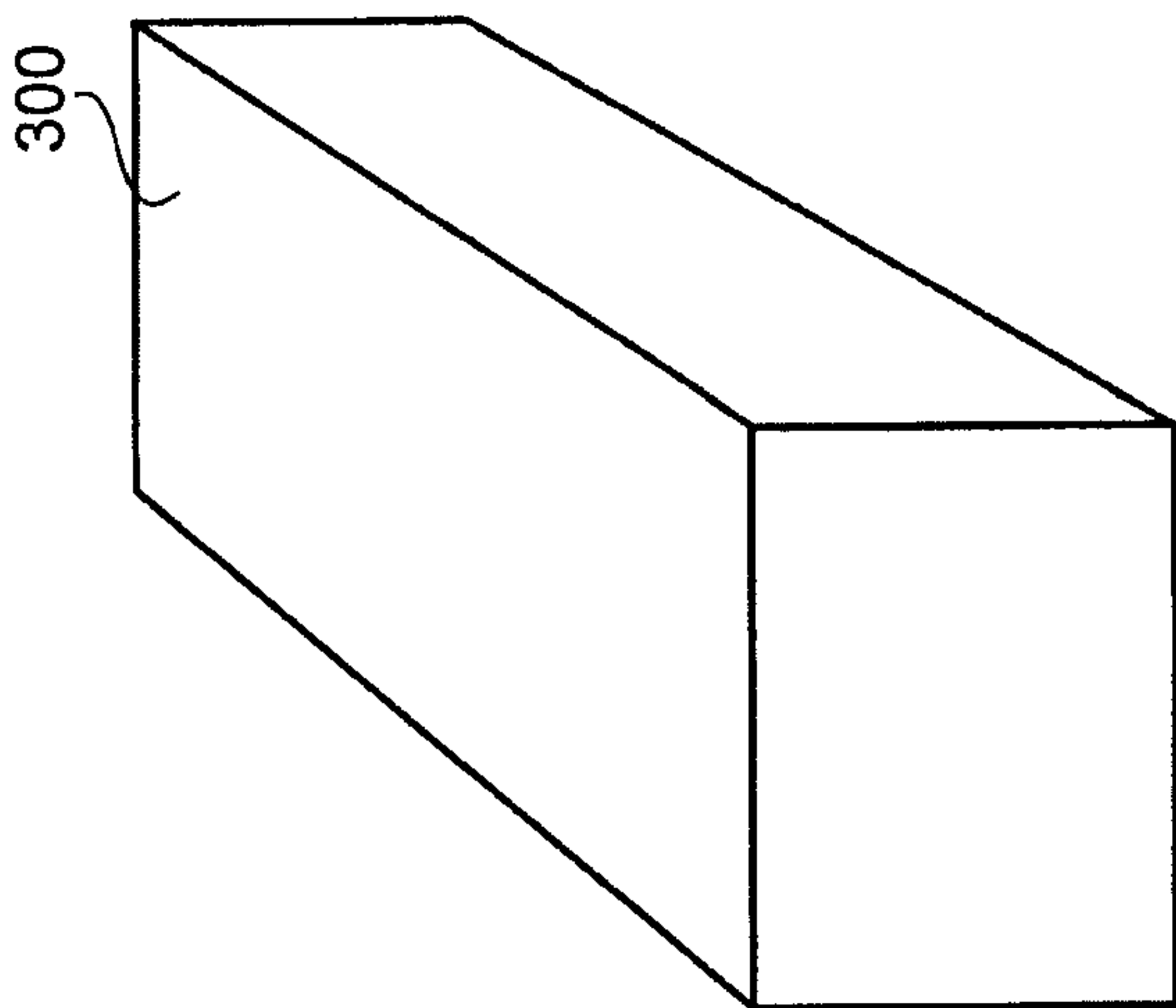


Fig. 3A

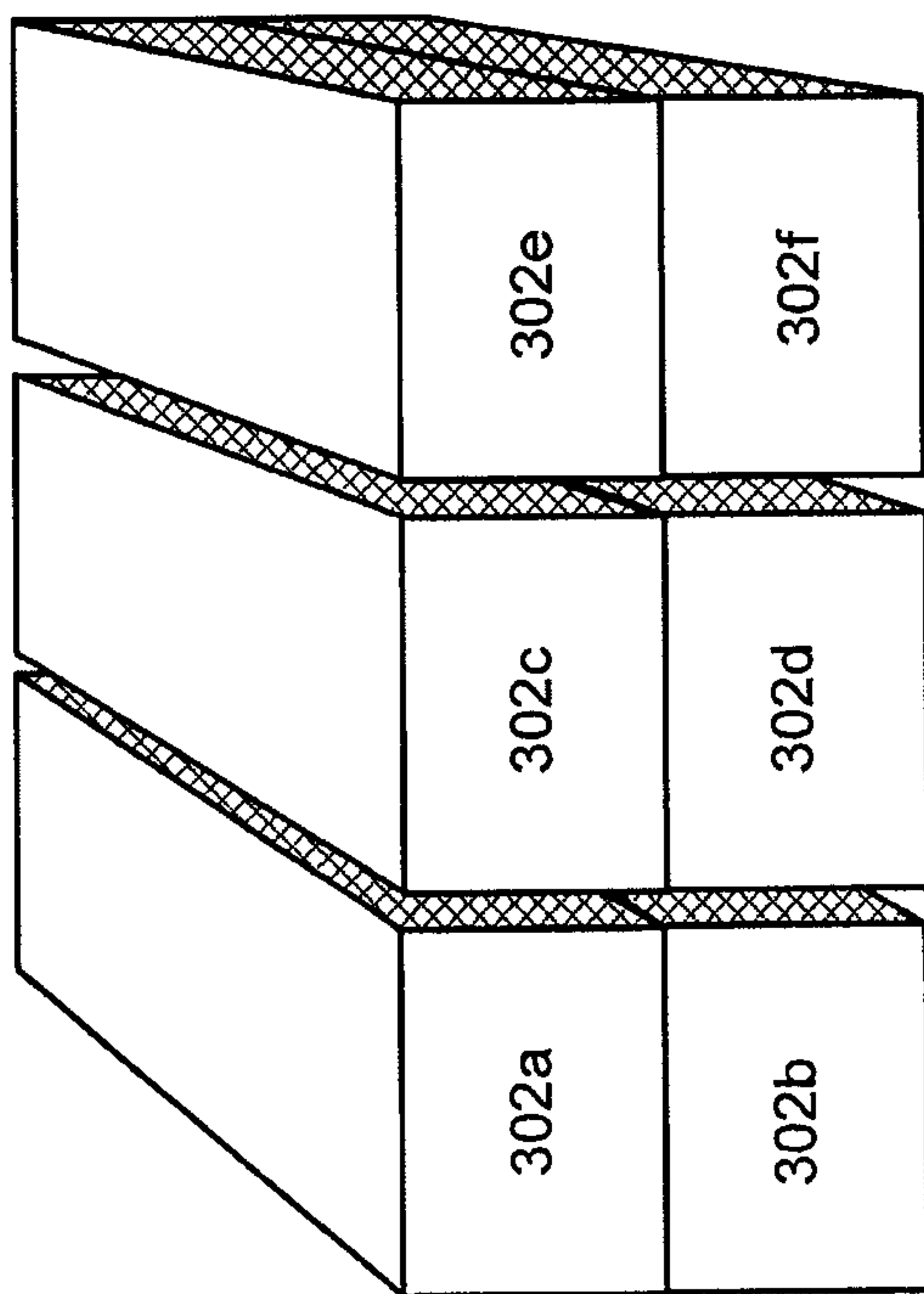


Fig. 3B

300

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400

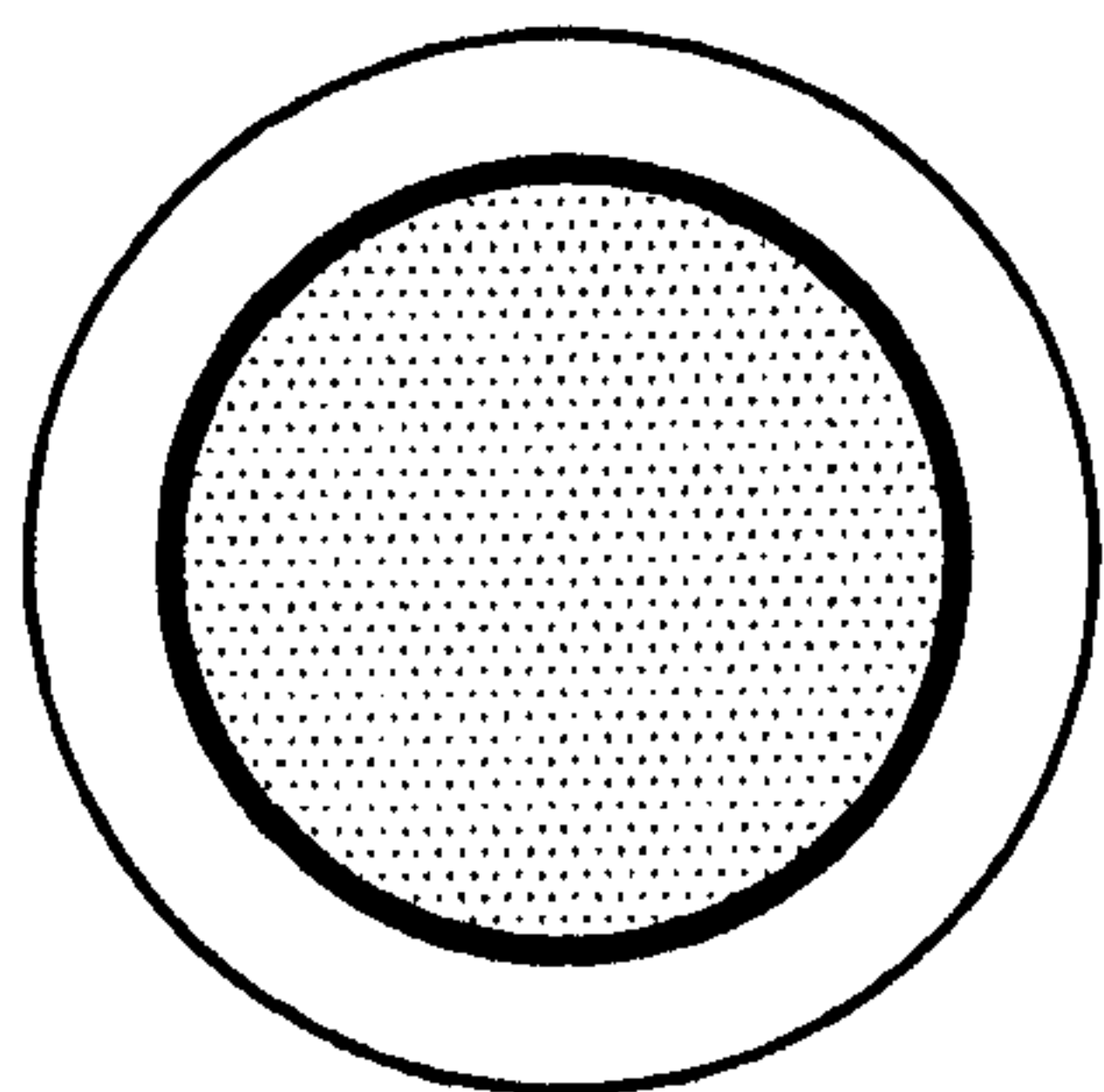


Fig. 4A

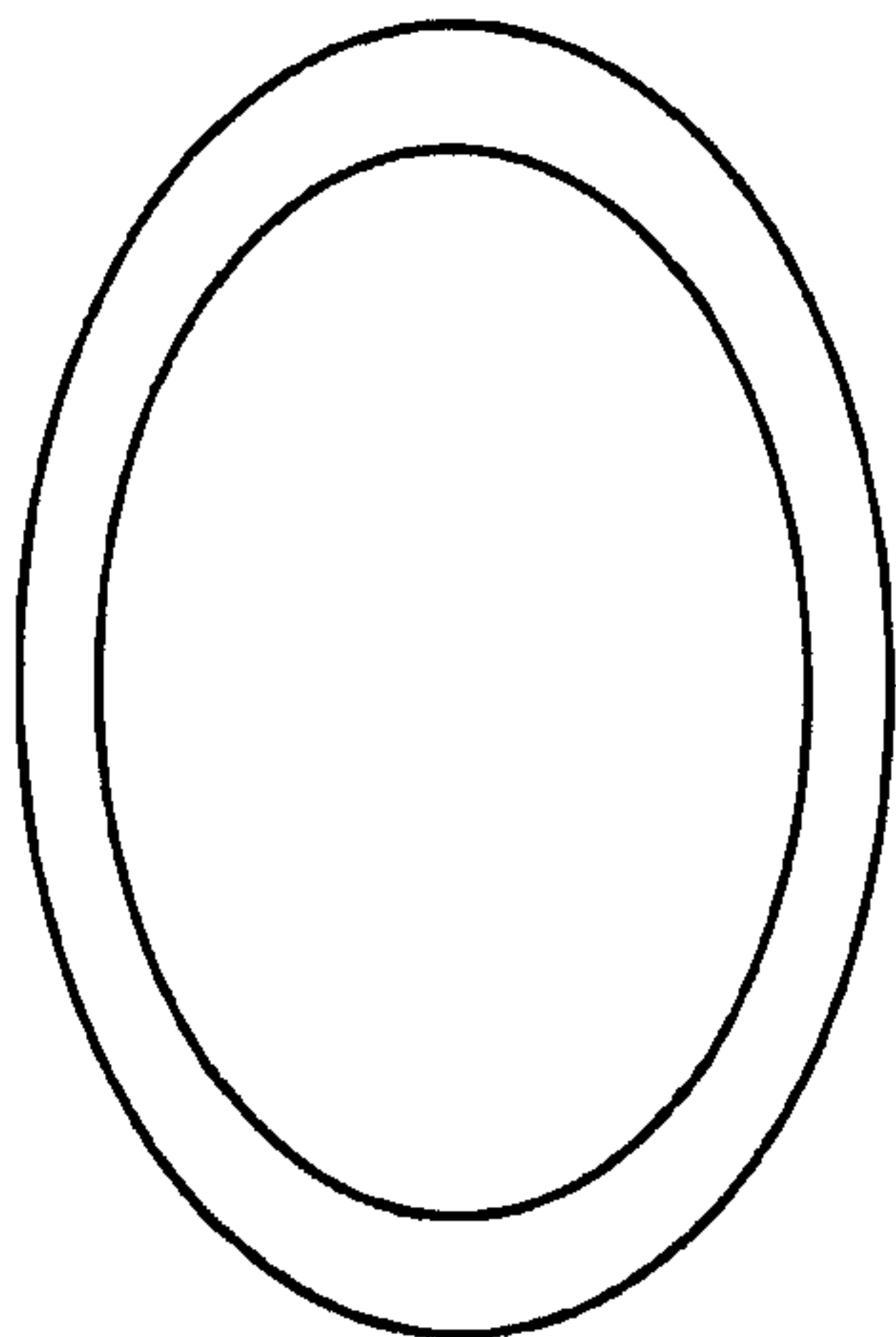


Fig. 4C

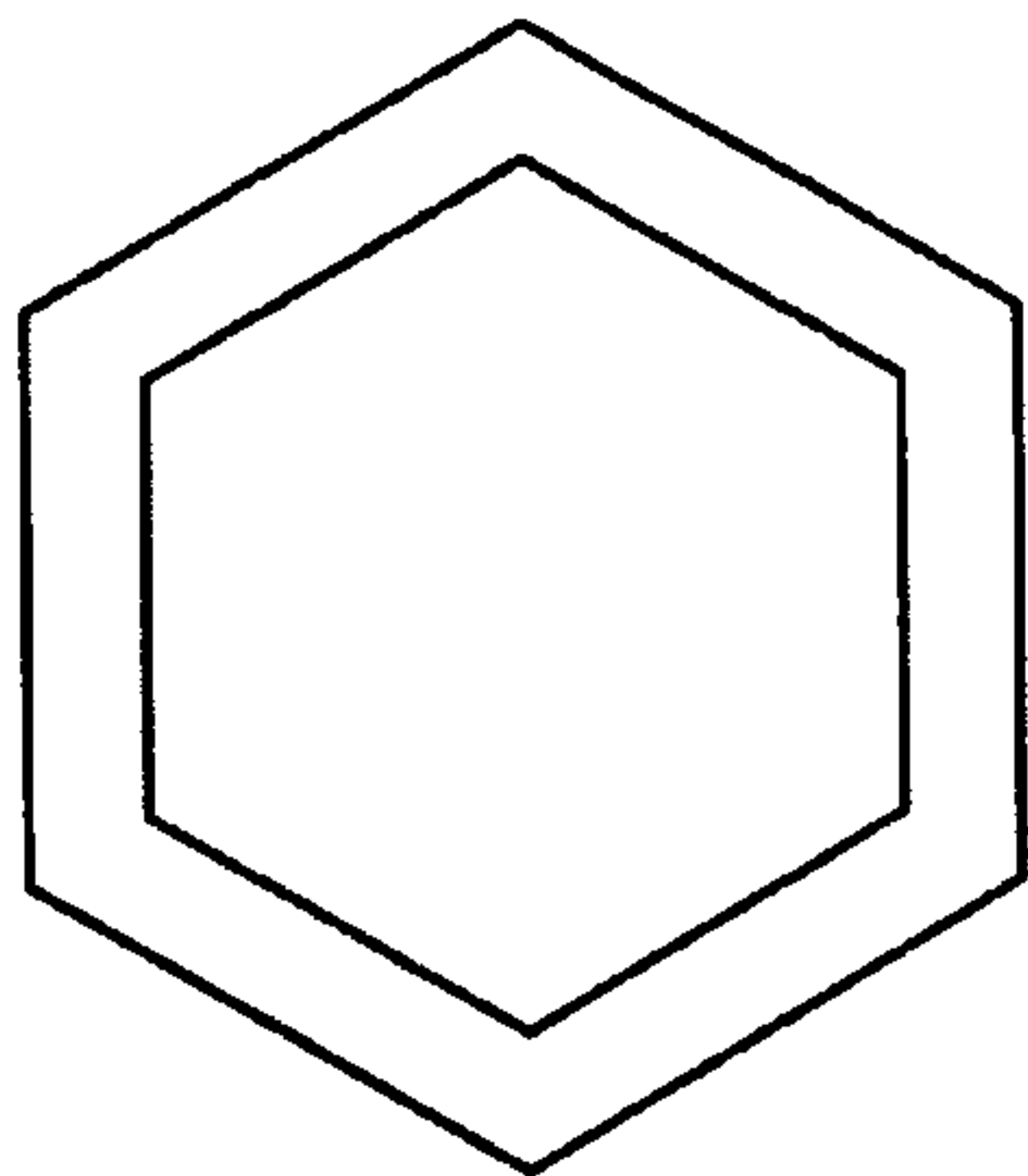


Fig. 4E

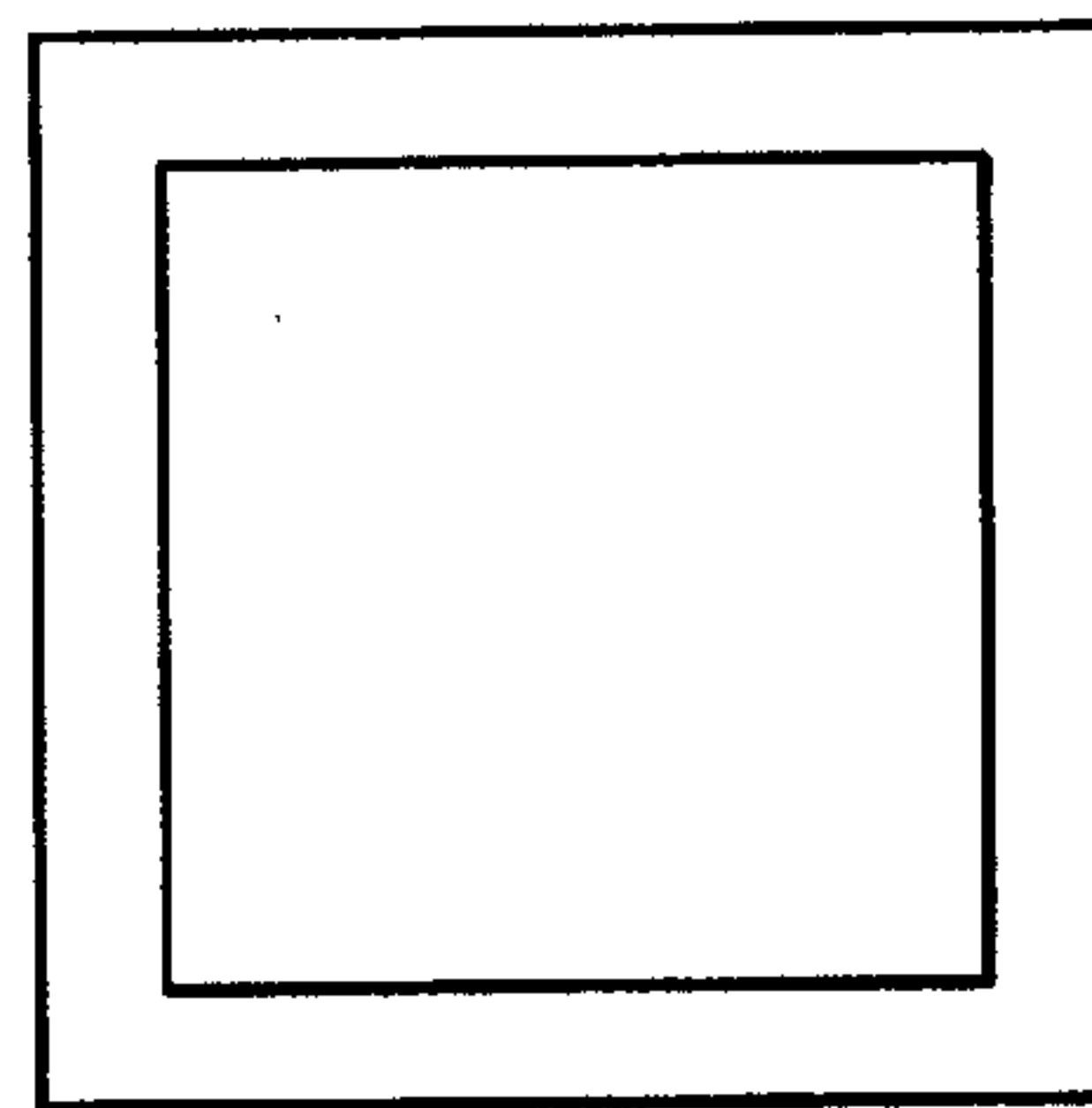


Fig. 4B

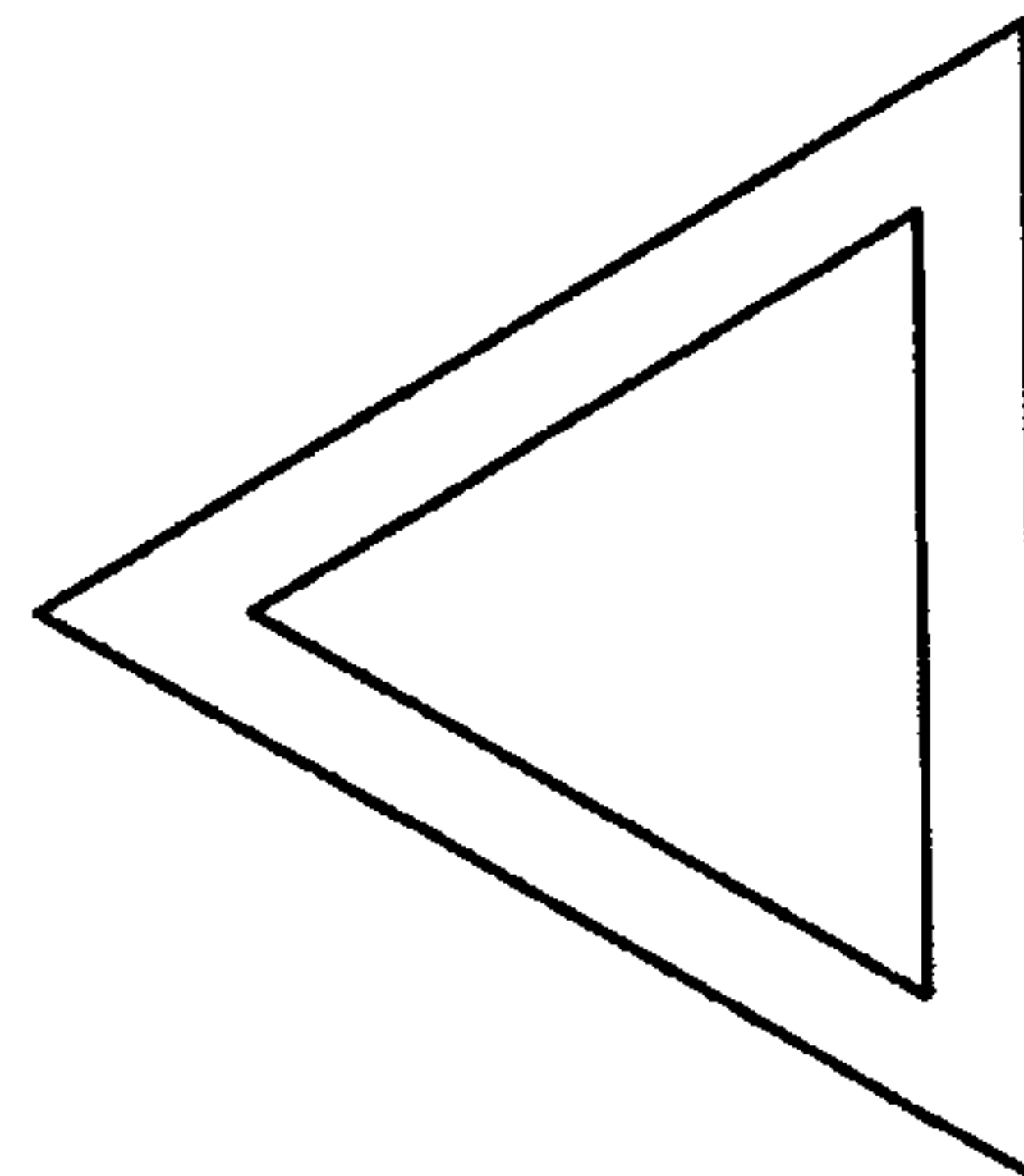


Fig. 4D

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504

500

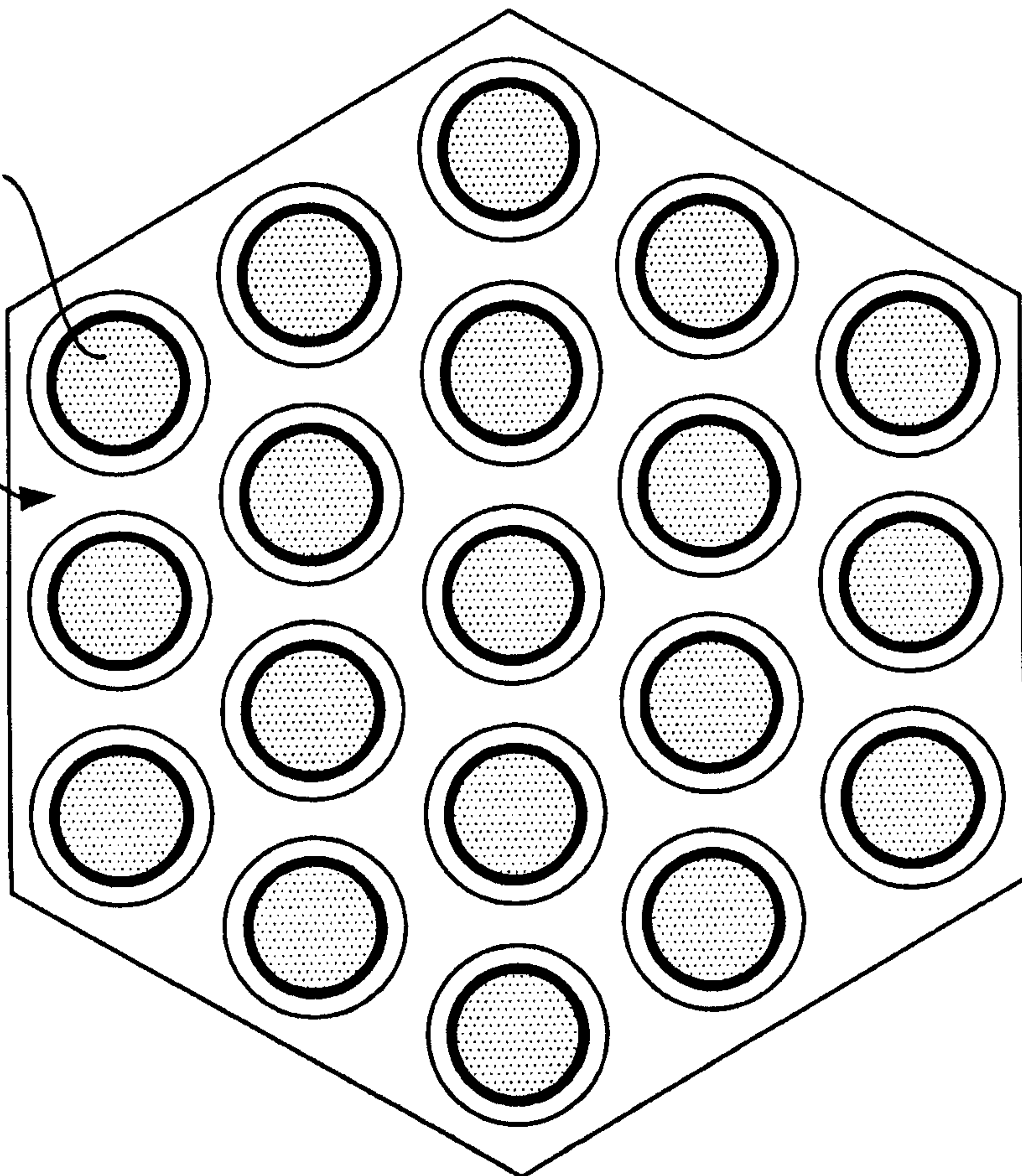


Fig. 5A

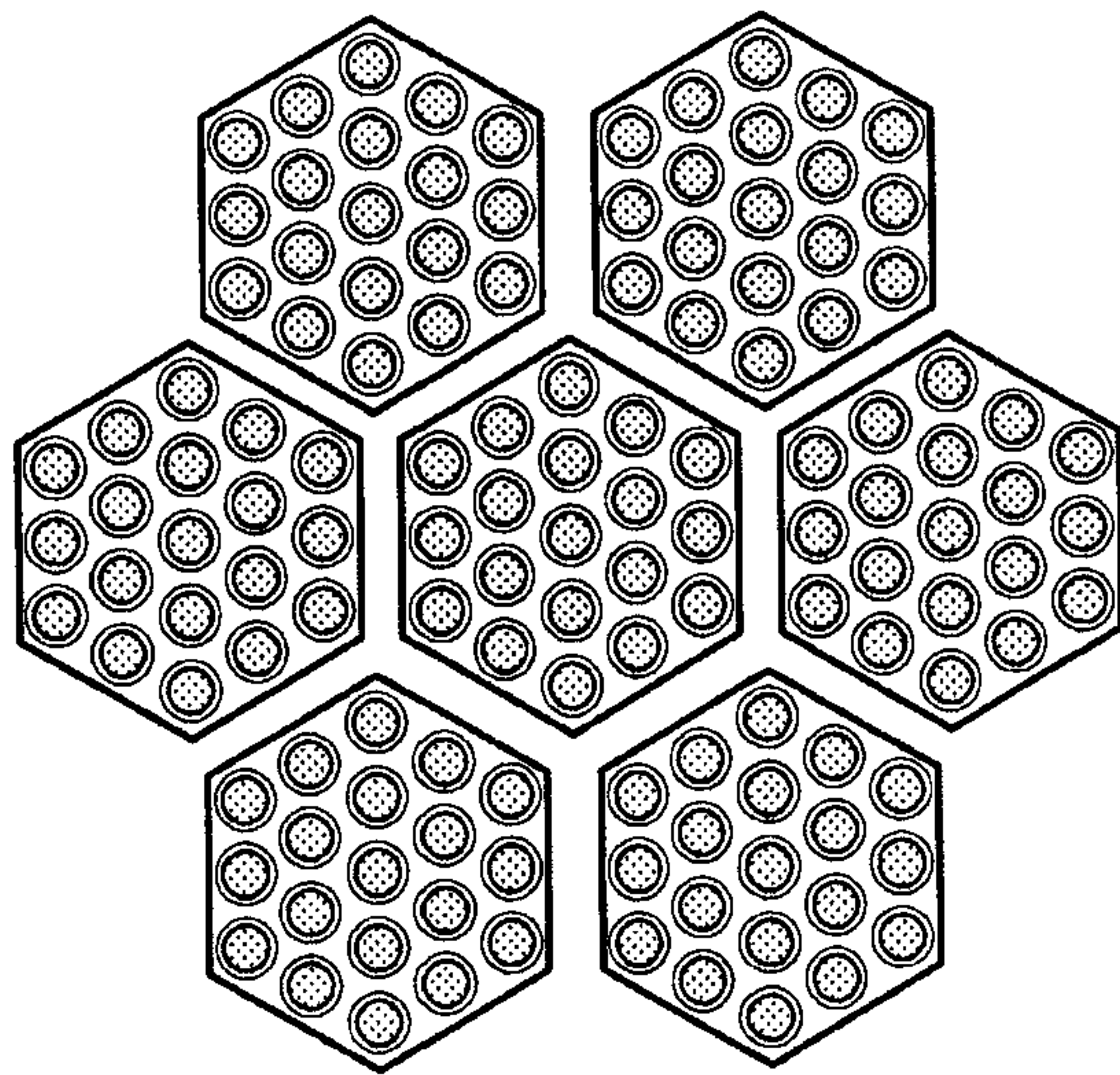


Fig. 5B

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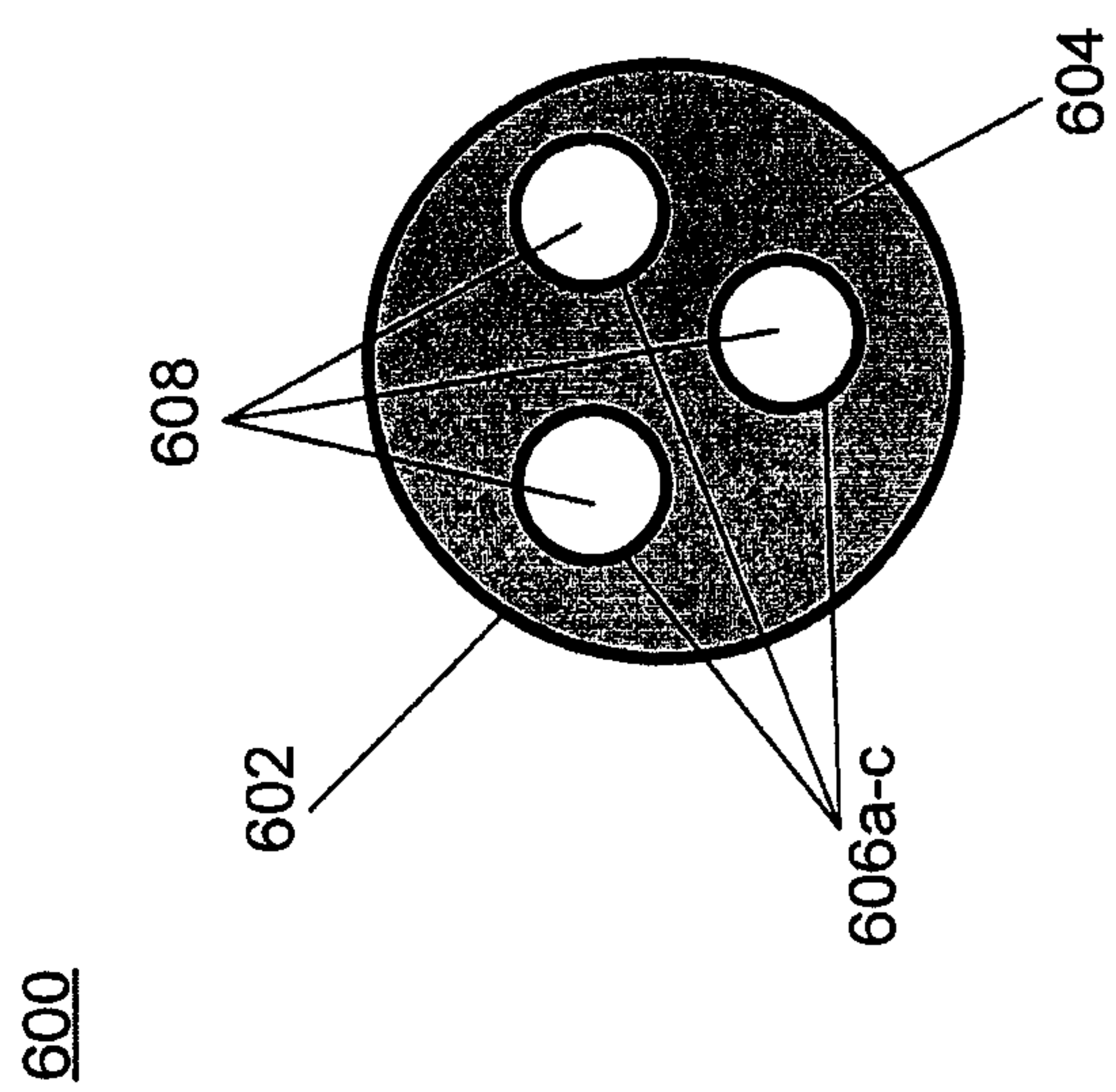


Fig. 6

100

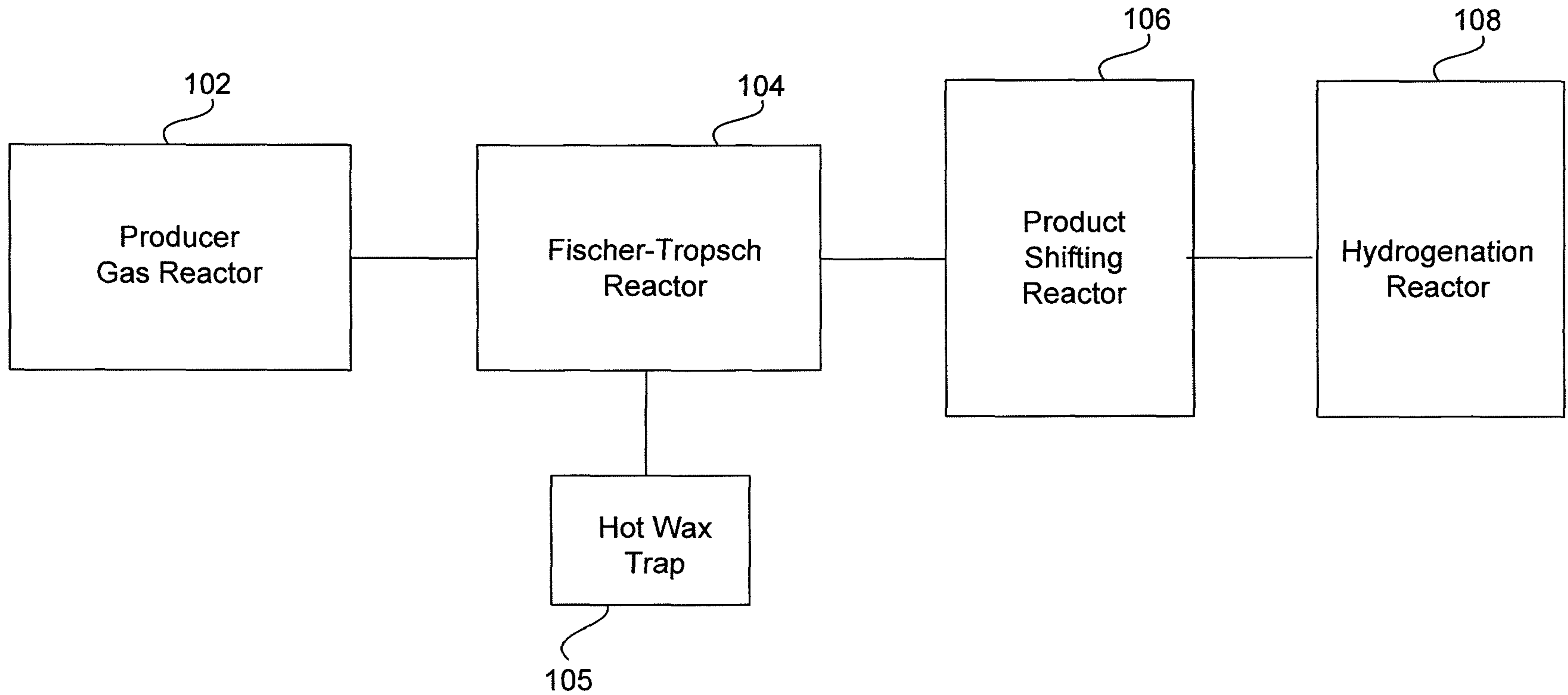


FIG. 1