#### (12) STANDARD PATENT

(11) Application No. AU 2013407175 B2

#### (19) AUSTRALIAN PATENT OFFICE

(54) Title

Method for preparing a light olefin using an oxygen-containing compound, and device for use thereof

(51) International Patent Classification(s)

**C07C 1/20** (2006.01)

C07C 11/02 (2006.01)

**B01J 8/26** (2006.01)

(21) Application No: **2013407175** 

(22) Date of Filing:

2013.12.03

(87) WIPO No: WO15/081484

(43) Publication Date:

2015.06.11

(44) Accepted Journal Date:

2017.06.15

(71) Applicant(s)

Dalian Institute of Chemical Physics, Chinese Academy of Sciences

(72) Inventor(s)

Liu, Zhongmin; Ye, Mao; Zhang, Tao; He, Changqing; Wang, Xiangao; Zhao, Yinfeng

(74) Agent / Attorney

Shelston IP Pty Ltd., Level 21, 60 Margaret Street, Sydney, NSW, 2000, AU

(56) Related Art

CN 101239870 A

AU 2013407180

CN 103193574 A

#### (12) 按照专利合作条约所公布的国际申请

## (19) 世界知识产权组织 国际局





#### (10) **国际公布号** WO 2015/081484 A1

(51) 国际专利分类号:

**C07C 1/20** (2006.01) **B01J 8/26** (2006.01)

C07C 11/02 (2006.01)

(21) 国际申请号: PCT/CN2013/088388

(22) 国际申请日: 2013年12月3日 (03.12.2013)

(25) 申请语言: 中文

(26) 公布语言: 中文

- (71) 申请人: 中国科学院大连化学物理研究所 (DALIAN INSTITUTE OF CHEMICAL PHYSICS, CHINESE ACADEMY OF SCIENCES) [CN/CN]; 中国辽宁省大连市中山路 457号, Liaoning 116023 (CN)。
- (72) **发明人**: **刘中民** (LIU, Zhongmin); 中国辽宁省大连市中山路 457号, Liaoning 116023 (CN)。 **叶茂** (YE, Mao); 中国辽宁省大连市中山路 457号, Liaoning 116023 (CN)。 **张涛** (ZHANG, Tao); 中国辽宁省大连市中山路 457号, Liaoning 116023 (CN)。 何长青 (HE, Changqing); 中国辽宁省大连市中山路 457号,

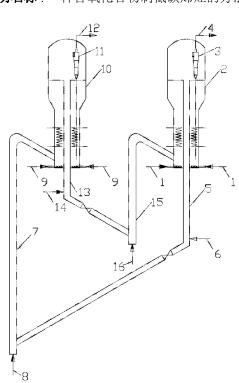
Liaoning 116023 (CN)。 **王贤高 (WANG, Xiangao)**; 中国辽宁省大连市中山路 457 号, Liaoning 116023 (CN)。 **赵银峰 (ZHAO, Yinfeng)**; 中国辽宁省大连市中山路 457 号, Liaoning 116023 (CN)。

- (74) 代理人: 中科专利商标代理有限责任公司 (CHINA SCIENCE PATENT & TRADEMARK AGENT LTD.); 中国北京市海淀区西三环北路 87 号 4-1105 室, Beijing 100089 (CN)。
- (81) 指定国 (除另有指明,要求每一种可提供的国家保护): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, 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, IR, IS, JP, KE, KG, 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, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW。

[见续页]

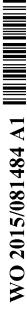
(54) Title: METHOD FOR PREPARING A LIGHT OLEFIN USING AN OXYGEN-CONTAINING COMPOUND, AND DEVICE FOR USE THEREOF

(54) 发明名称: 一种含氧化合物制低碳烯烃的方法及其使用的设备



|劉 | / FIG. 1

- (57) Abstract: The present invention relates to a method for preparing a light olefin using an oxygen-containing compound, and device for use thereof. More specifically, the present invention provides a method for using an oxygen-containing compound to prepare a light olefin, taking methanol and/or dimethyl ether as main starting materials, using a multi-stage (n≥2) dense phase fluidized bed reactor and a multi-stage (m≥2) catalyst regenerator; the invention solves the problems in the prior art of the uniformity of catalyst carbon deposition and carbon content being difficult to control and light olefin selectivity being low.
- (57) 摘要: 本发明涉及含氧化合物制低碳烯烃的方法及其使用的设备。更具体地,本发明提供一种含氧化合物制低碳烯烃的方法,以甲醇和/或二甲醚为主要原料,采用多级(n≥2)密相流化床反应器和多级(m≥2)催化剂再生器,解决了现有技术中催化剂积碳量和碳含量均匀性难以控制以及低碳烯烃选择性较低的问题。



(84) **指定国** (除另有指明,要求每一种可提供的地区保护): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), 欧亚 (AM, AZ, BY, KG, KZ, RU, TJ, TM), 欧洲 (AL, 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, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG,

CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG)  $_{\circ}$ 

#### 本国际公布:

包括国际检索报告(条约第21条(3))。

10

15

20

25

30

# Method for preparing a light olefin using an oxygen-containing compound, and device for use thereof

#### **Technical field**

The present invention relates to a method for preparing a light olefin using an oxygen-containing compound, and a device for use thereof.

#### **Background**

Light olefins, i.e. ethylene and propylene, are two important kinds of basic chemical raw materials, and the demand thereof is increasing. Generally, ethylene and propylene are produced via a petroleum scheme. However, the costs for producing ethylene and propylene from petroleum resources are increasing due to limited supply and relatively high price of petroleum resources. In recent years, techniques for preparing ethylene and propylene by converting substituent raw materials have been greatly developed. More and more attentions have been paid to the process of methanol-to-olefins (MTO), and the production scale of megatonnage has been achieved. As the world economy develops, the demand for light olefins, particularly propylene, is increasing day by day. It is reported as the analysis of CMAI Corporation that the demand for ethylene will increase at an average rate of 4.3% per year and the demand for propylene will increase at an average rate of 4.4% per year until 2016. Due to high-speed increase of the economy in China, all of the annual increase rates of the demand for ethylene and propylene in China exceed the average level of the world.

In early 1980s, UCC Corporation successfully developed SAPO series molecular sieves. Among others, SAPO-34 molecular sieve catalyst exhibits excellent catalytic performance when it is used in MTO reaction, and has very high selectivity for light olefins and very high activity. However, after the catalyst has been used for a period of time, the activity is lost due to carbon deposition. A remarkable induction period is present in the use of the

SAPO-34 molecular sieve catalyst. In the induction period, the selectivity for olefins is relatively low and the selectivity for alkanes is relatively high. As the reaction time increases, the selectivity for light olefins gradually increases. After the induction period, the catalyst maintains high selectivity and high activity in a certain period of time. With further prolong of the time, however, the activity of the catalyst rapidly decreases.

US6166282 discloses a technique and a reactor for converting methanol to light olefins, which use a fast fluidized bed reactor, wherein after the completion of a reaction in a dense phase reaction zone having a relatively low gas speed, the gas phase rises to a fast separation zone having an inner diameter which rapidly becomes smaller, and most of the entrained catalyst is preliminarily separated using a special gas-solid separation apparatus. Since the product gas and the catalyst are rapidly separated after reaction, a secondary reaction is effectively prevented. Upon analog computation, the inner diameter of the fast fluidized bed reactor and the catalyst inventory required are both greatly reduced, compared to the conventional bubbling fluidized bed reactors. However, the carbon based yields of light olefins in this method are all typically about 77%, and there are problems concerning relatively low yields of light olefins.

CN101402538B discloses a method for increasing the yield of light olefins. This method provides a second reaction zone on the upper part of a first reaction zone for converting methanol to light olefins, and the diameter of the second reaction zone is greater than that of the first reaction zone to increase the residence time of the product gas from the outlet of the first reaction zone in the second reaction zone, such that the unreacted methanol, the generated dimethyl ether, and hydrocarbons having 4 or more carbons continue to react so as to achieve the object of increasing the yield of light olefins. This method may increase the yield of light olefins to some extent. However, since the catalyst come out from the first reaction zone has already carried a relatively great amount of deposited carbon and relatively high

10

15

20

25

30

catalyst activity is required to crack hydrocarbons having 4 or more carbons, the conversion efficiencies of hydrocarbons having 4 or more carbons in the second reaction zone in this method are still relatively low, leading to a lower yield of light olefins.

CN102276406A discloses a method for increasing the production of propylene. This technique provides three reaction zones, wherein a first fast bed reaction zone is used for converting methanol to olefins, and a lift pipe reaction zone and a second fast bed reaction zone are connected in series to convert ethylene, hydrocarbons having 4 or more carbons, and unreacted methanol or dimethyl ether. In this patent application, the residence times of substances, such as hydrocarbons having 4 or more carbons, etc., in the lift pipe reaction zone and in the second fast bed reaction zone are relatively short and the conversion efficiencies are relatively low, such that the yield of propylene is relatively low.

CN102875289A discloses a fluidized bed reaction device with a lift pipe reactor arranged therein, which is used for increasing the yield of light olefins. A first raw material is passed into a fluidized bed reaction zone and is brought into contact with a catalyst to generate a product comprising light olefins, and at the meanwhile a spent catalyst is formed; a part of the spent catalyst is passed into a regenerator for regeneration to form a regenerated catalyst, and the other part of the spent catalyst is passed into a lift pipe with an outlet end located inside the reaction zone and is brought into contact with a second raw material so as to lift the spent catalyst into the reaction zone; and the regenerated catalyst is returned to the reaction zone of the fluidized bed reactor. Since the reaction device disclosed in this patent application does not comprise a stripping portion, the spent catalyst will be passed into the regenerator with carrying a part of the product gas, which is combusted with oxygen to reduce the yield of light olefins.

The technique for preparing olefins from methanol disclosed in CN102875296A provides three reaction zones, which are a fast bed, a downer,

10

15

20

25

30

and a lift pipe. Since the catalyst is circulated among the regenerator, the fast bed, the lift pipe, and the downer, the flow direction is extremely complicated, the distribution and the control of the flow rate are extremely difficult, and the activity of catalyst greatly varies.

As well known in the art, the selectivity for light olefins is closely associated with the amount of carbon deposition on the catalyst. A certain amount of carbon deposition on SAPO-34 catalyst is needed to ensure a high selectivity for light olefins. Main reactors used in current MTO process are fluidized beds. The fluidized bed is close to a perfect mixing flow reactor, which has a wide distribution of carbon deposition on catalyst and is not advantageous for increasing the selectivity for light olefins. Since the catalyst-to-alcohol ratio is very small and the coke yield is relatively low in the MTO process, in order to achieve a lager and controllable catalyst circulation volume, it is required to control the amount of carbon deposition and the uniformity of carbon content on the catalyst to a certain level in the regeneration zone, thereby achieving the object of controlling the amount of carbon deposition and the uniformity of carbon content on the catalyst in the reaction zone. Therefore, it is a key technique in the MTO process to control the amount of carbon deposition and the uniformity of carbon content of the catalyst in the reaction zone to a certain level.

In order to solve the problems described above, some researchers propose the techniques, such as providing an upper and a lower reaction zones in a fluidized bed, two fluidized beds connected in series, and a fluidized bed, a lift pipe, and a downer connected in series, etc. These preliminarily disclose methods for controlling the amount of carbon deposition and the uniformity of carbon content of the catalyst, and certain advantageous effects have been obtained. However, the complexity and the difficulty for controlling the MTO process are increased at the meanwhile. The present invention proposes a solution in which a plurality of secondary reaction zones (regeneration zones) are formed by providing inner members in a dense phase fluidized bed, to

10

15

20

25

30

solve the problem of controlling the amount of carbon deposition and the uniformity of carbon content of the catalyst so as to increase the selectivity for light olefins.

Any discussion of the prior art throughout the specification should in no way be considered as an admission that such prior art is widely known or forms part of common general knowledge in the field.

#### Summary of the invention

It is an object of the present invention to overcome or ameliorate at least one of the disadvantages of the prior art, or to provide a useful alternative.

An object of a preferred embodiment of the invention is to provide a new method for increasing the selectivity for light olefins. This method is used in the production of light olefins, and has the advantages of good uniformity of carbon deposition on catalyst, relatively high yield of light olefins, and good economical efficiency of the production process of light olefins.

Unless the context clearly requires otherwise, throughout the description and the claims, the words "comprise", "comprising", and the like are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense; that is to say, in the sense of "including, but not limited to".

In one aspect, the present invention provides a method for preparing a light olefin using an oxygen-containing compound, comprising the following steps:

step a) in which a raw material comprising the oxygen-containing compound is introduced in parallel from n feeding branch lines into 1st to nth secondary reaction zones in a dense phase fluidized bed reactor, and is brought into contact with a catalyst to generate a light olefin product-containing stream and a spent catalyst, wherein said catalyst is sequentially passed through 1st to nth secondary reaction zones, with the carbon content thereof increasing gradually, and wherein said dense phase fluidized bed reactor is divided by a material flow controller into n secondary reaction zones;

step b) in which the light olefin product-containing stream flowed out from

10

15

20

25

30

the 1<sup>st</sup> to n<sup>th</sup> secondary reaction zones is separated from the spent catalyst that it carries; said light olefin product-containing stream is passed into a product separation section, and after separation and purification, a light olefin product is obtained; the isolated spent catalyst is passed into the n<sup>th</sup> secondary reaction zone; and

step c) in which the spent catalyst flowed out from the n<sup>th</sup> secondary reaction zone, after being stripped and lifted, is passed into a dense phase fluidized bed regenerator for regeneration; said spent catalyst is sequentially passed through 1<sup>st</sup> to m<sup>th</sup> secondary regeneration zones; a regeneration medium is introduced in parallel from m feeding branch lines of regeneration zone into the 1<sup>st</sup> to m<sup>th</sup> secondary regeneration zones; the spent catalyst is brought into contact with the regeneration medium, with the carbon content thereof decreasing gradually; after the completion of the regeneration, the catalyst is returned back to the 1<sup>st</sup> secondary reaction zone via stripping and lifting; wherein the dense phase fluidized bed regenerator is divided by a material flow controller into m secondary regeneration zones;

wherein  $n \ge 2$  and  $m \ge 2$ .

In a preferred embodiment,  $8 \ge n \ge 3$  and  $8 \ge m \ge 3$ .

In a preferred embodiment, in the dense phase fluidized bed reactor, the apparent linear velocity of gas in the material flow controller is less than or equals to the minimum fluidizing velocity of the catalyst.

In a preferred embodiment, in the dense phase fluidized bed regenerator, the apparent linear velocity of gas in the material flow controller is less than or equals to the minimum fluidizing velocity of the catalyst.

In a preferred embodiment, the catalyst comprises SAPO-34 molecular sieve.

In a preferred embodiment, the reaction conditions of the reaction zone in the dense phase fluidized bed are as follows: the apparent linear velocity of gas is 0.1-1.5 m/s, reaction temperature is 400-550 °C, the bed density is 200-1200 kg/m<sup>3</sup>.

10

15

20

25

30

In a preferred embodiment, the average carbon deposition amount of the catalyst is increased sequentially in the 1<sup>st</sup> to n<sup>th</sup> secondary reaction zones of the dense phase fluidized bed, wherein the average carbon deposition amount of the catalyst in the 1<sup>st</sup> secondary reaction zone is 0.5-3 wt%, the average carbon deposition amount of the catalyst in the n<sup>th</sup> secondary reaction zone is 7-10 wt%.

In a preferred embodiment, the reaction conditions in the dense phase fluidized bed regeneration zone are as follows: the apparent linear velocity of gas is 0.1-1.5 m/s, the regeneration temperature is 500-700 °C, and the bed density is 200-1200 kg/m<sup>3</sup>.

In a preferred embodiment, the average carbon deposition amount of the catalyst is decreased sequentially from the 1<sup>st</sup> to m<sup>th</sup> secondary regeneration zones of the dense phase fluidized bed regeneration zone, wherein the average carbon deposition amount of the catalyst in the 1<sup>st</sup> secondary regeneration zone is 3-10 wt%, and the average carbon deposition amount of the catalyst in the m<sup>th</sup> secondary regeneration zone is 0-3 wt%.

In a preferred embodiment, the oxygen-containing compound is methanol and/or dimethyl ether; the light olefin is any one of ethylene, propylene or butylenes, or a mixture thereof; and the regeneration medium is any one of air, oxygen-deficient air or water vapor, or a mixture thereof.

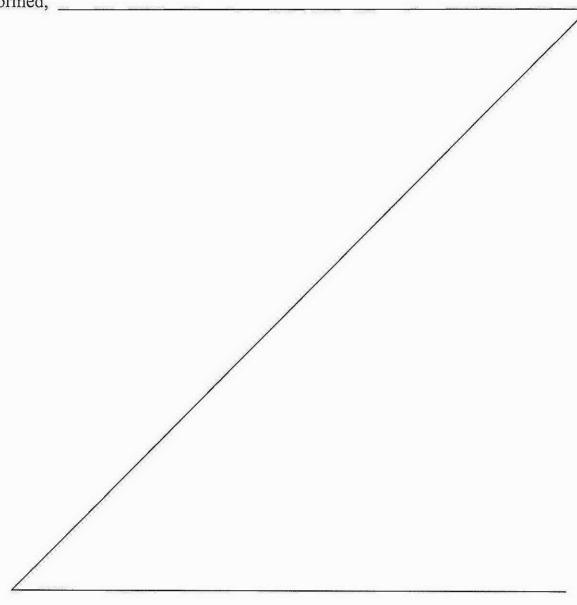
In another aspect, the present invention provides a dense phase fluidized bed reactor for carrying out the above method, said dense phase fluidized bed reactor comprising a reaction zone, a gas-solid separation zone, and a stripping zone, characterized in that said reaction zone is divided by a material flow controller into n secondary reaction zones, wherein  $n \ge 2$ .

In another aspect, the present invention provides a dense phase fluidized bed regenerator for carrying out the above method, said dense phase fluidized bed regenerator comprising a regeneration zone, a gas-solid separation zone, and a stripping zone, characterized in that said regeneration zone is divided by a material flow controller into m secondary regeneration zones, wherein  $m \ge 2$ .

10

In another aspect, the present invention provides a product produced by the method of the invention.

The advantageous effects of the preferred embodiments of the present invention include, but are not limited to, the following aspects: (1) the dense phase fluidized bed has a relatively high bed density, a relatively low catalyst velocity, and a low abrasion; (2) the gas velocity in the material downward flow pipe of the material flow controller is less than or equals to the minimal fluidization velocity of the catalyst and the catalyst is in a dense phase packing state, such that a unidirectional dense phase conveying stream of the catalyst is formed,



10

15

20

25

30

the backmixing of catalyst between adjacent secondary reaction zones (or adjacent secondary regeneration zones) is prevented, and the distribution of residence time is narrow; (3) the heat extraction member in the material flow controller has an effect of controlling the temperature of the reaction zone; (4) the reaction zone is divided into n secondary reaction zones by the material flow controller and the catalyst sequentially passes through the 1<sup>st</sup> secondary reaction zone to the n<sup>th</sup> secondary reaction zone, such that the distribution of residence time is narrow and the uniformity of carbon content of the spent catalyst is greatly increased; (5) the regeneration zone is divided into m secondary regeneration zones by the material flow controller and the catalyst sequentially passes through the 1st secondary regeneration zone to the mth secondary regeneration zone, such that the distribution of residence time is narrow and the uniformity of carbon content of the regenerated catalyst is greatly increased; (6) relatively precise control of carbon content of the regenerated catalyst and the spent catalyst is achieved, the distribution of carbon content is relatively uniform, the selectivity for light olefins is increased, and the carbon content may be regulated as needed to optimize the ratio of propylene/ethylene; (7) since the distribution of carbon content of the catalyst is relatively uniform, the catalyst inventory required in the reaction zone decreases; (8) the configuration of a plurality of secondary reaction zones facilitates the achievement of large-scale reactors.

#### **Description of figures**

Figure 1 is a schematic flow chart of the method in the present invention;

Figure 2 is a structural schematic diagram of the dense phase fluidized bed comprising 4 secondary reaction zones in the present invention, wherein the arrows in the A-A sectional view show the flow direction of the catalyst between the secondary reaction zones;

Figure 3 is a structural schematic diagram of the dense phase fluidized bed comprising 4 secondary regeneration zones in the present invention,

10

15

20

wherein the arrows in B-B sectional view show the flow direction of the catalyst between the secondary regeneration zones;

Figure 4 is a structural schematic diagram of the stripper in the present invention;

Figure 5 is a structural schematic diagram of the material flow controller in the present invention.

The reference signs of the figures are illustrated as follows:

1: reactor feed line; 1-1: feeding branch line of 1<sup>st</sup> secondary reaction zone; 1-2: feeding branch line of 2<sup>nd</sup> secondary reaction zone; 1-3: feeding branch line of 3<sup>rd</sup> secondary reaction zone; 1-4: feeding branch line of 4<sup>th</sup> secondary reaction zone; 2: dense phase fluidized bed reactor; 2-1: 1st secondary reaction zone; 2-2: 2<sup>nd</sup> secondary reaction zone; 2-3: 3<sup>rd</sup> secondary reaction zone; 2-4: 4th secondary reaction zone; 3: cyclone separator; 4: product material line; 5: stripper; 6: water vapor line; 7: lift pipe; 8: lifting gas line; 9: regenerator feed line; 9-1: feeding branch line of 1<sup>st</sup> secondary regeneration zone; 9-2: feeding branch line of 2<sup>nd</sup> secondary regeneration zone; 9-3: feeding branch line of 3<sup>rd</sup> secondary regeneration zone; 9-4: feeding branch line of 4<sup>th</sup> secondary regeneration zone; 10: dense phase fluidized bed regenerator; 10-1: 1<sup>st</sup> secondary regeneration zone; 10-2: 2<sup>nd</sup> secondary regeneration zone; 10-3: 3<sup>rd</sup> secondary regeneration zone; 10-4: 4<sup>th</sup> secondary regeneration zone; 11: cyclone separator; 12: exhaust gas line; 13: stripper; 14: water vapor line; 15: lift pipe; 16: lifting gas line; 17: material flow controller; 18: material overflow port; 19: partition plate; 20: orifice; 21: material downward flow pipe; 22: bottom baffle; 23: heat extraction member.

25

30

#### **Description of the preferred embodiments**

In order to increase the selectivity for light olefins in the process of preparation of a light olefin using an oxygen-containing compound, the present invention provides a method for preparing a light olefin using an oxygen-containing compound, comprising the following steps:

10

15

20

25

30

- a) a step in which a raw material comprising the oxygen-containing compound is introduced in parallel from n feeding branch lines into 1<sup>st</sup> to n<sup>th</sup> secondary reaction zones in a dense phase fluidized bed reactor, and is brought into contact with a catalyst to generate a light olefin product-containing stream and a spent catalyst, wherein said catalyst is sequentially passed through 1<sup>st</sup> to n<sup>th</sup> secondary reaction zones, with the carbon content thereof increasing gradually, and wherein said dense phase fluidized bed reactor is divided by a material flow controller into n secondary reaction zones;
- b) a step in which the light olefin product-containing stream flowed out from the 1<sup>st</sup> to n<sup>th</sup> secondary reaction zones is separated from the spent catalyst that it carries; said light olefin product-containing stream is passed into a product separation section, and after separation and purification, a light olefin product is obtained; the isolated spent catalyst is passed into the n<sup>th</sup> secondary reaction zone; and
  - c) a step in which the spent catalyst flowed out from the n<sup>th</sup> secondary reaction zone, after being stripped and lifted, is passed into a dense phase fluidized bed regenerator for regeneration; said spent catalyst is sequentially passed through 1<sup>st</sup> to m<sup>th</sup> secondary regeneration zones; a regeneration medium is introduced in parallel from m feeding branch lines of regeneration zone into the 1<sup>st</sup> to m<sup>th</sup> secondary regeneration zones; the spent catalyst is brought into contact with the regeneration medium, with the carbon content thereof decreasing gradually; after the completion of the regeneration, the catalyst is returned back to the 1<sup>st</sup> secondary reaction zone via stripping and lifting; wherein the dense phase fluidized bed regenerator is divided by a material flow controller into m secondary regeneration zones.

Wherein  $n\ge 2$ , preferably  $8\ge n\ge 3$ ;  $m\ge 2$ , preferably  $8\ge m\ge 3$ .

Preferably, in the dense phase fluidized bed reactor, the apparent linear velocity of gas in the material flow controller is less than or equals to the

10

15

20

25

30

minimum fluidizing velocity of the catalyst.

Preferably, in the dense phase fluidized bed regenerator, the apparent linear velocity of gas in the material flow controller is less than or equals to the minimum fluidizing velocity of the catalyst.

Preferably, the catalyst comprises SAPO-34 molecular sieve.

Preferably, the reaction conditions of the reaction zone in the dense phase fluidized bed are as follows: the apparent linear velocity of gas is 0.1-1.5 m/s, reaction temperature is 400-550 °C, the bed density is 200-1200 kg/m<sup>3</sup>; the average carbon deposition amount of the catalyst in the 1<sup>st</sup> secondary reaction zone is 0.5-3 wt%, and the average carbon deposition amount of the catalyst in the n<sup>th</sup> secondary reaction zone is 7-10 wt%.

Preferably, the reaction conditions in the dense phase fluidized bed regeneration zone are as follows: the apparent linear velocity of gas is 0.1-1.5 m/s, the regeneration temperature is 500-700 °C, and the bed density is 200-1200 kg/m³; the average carbon deposition amount of the catalyst is decreased sequentially from the 1<sup>st</sup> to m<sup>th</sup> secondary regeneration zones, the average carbon deposition amount of the catalyst in the 1<sup>st</sup> secondary regeneration zone is 3-10 wt%, and the average carbon deposition amount of the catalyst in the m<sup>th</sup> secondary regeneration zone is 0-3 wt%.

Preferably, the oxygen-containing compound is methanol and/or dimethyl ether; the light olefin is any one of ethylene, propylene or butylene, or a mixture thereof; the regeneration medium is any one of air, oxygen-deficient air or water vapor, or a mixture thereof.

The technical solution provided in the present invention may further comprises:

- (1) providing a dense phase fluidized bed reactor, comprising a reaction zone, a gas-solid separation zone, and a stripping zone, the reaction zone being divided by a material flow controller into n secondary reaction zones, wherein n≥2;
  - (2) providing a dense phase fluidized bed regenerator, comprising a

10

15

20

25

30

regeneration zone, a gas-solid separation zone, and a stripping zone, the regeneration zone being divided by a material flow controller into m secondary regeneration zones, wherein m $\geq$ 2.

Preferably, the raw material comprising an oxygen-containing compound is introduced into the dense phase fluidized bed reactor and is brought into contact with regenerated catalyst, resulting in a light olefin-containing product and a carbon-containing spent catalyst, meanwhile, the regenerated catalyst is sequentially passed through 1<sup>st</sup> to n<sup>th</sup> secondary reaction zones, with the carbon content thereof increasing gradually.

Preferably, via stripping and lifting, the spent catalyst flowing out from the n<sup>th</sup> secondary reaction zone is passed into the dense phase fluidized bed regenerator for regeneration, the spent catalyst is sequentially passed through 1<sup>st</sup> to m<sup>th</sup> secondary regeneration zone, and is brought into contact with the regeneration medium, with the carbon content thereof gradually decreasing, and then the catalyst is returned back to 1<sup>st</sup> secondary reaction zone via stripping and lifting.

Preferably, the stream of the light olefin product is passed into separation section after separation with spent catalyst, and the isolated spent catalyst is passed into n<sup>th</sup> secondary reaction zone.

In a specific embodiment, the schematic flow chart for preparing a light olefin using a oxygen-containing compound in the present invention is as shown in Fig. 1. The raw material comprising the oxygen-containing compound is introduced from reactor feed line (1) and breach lines (1-1, ....., 1-n) thereof in parallel into secondary reaction zones (2-1, ....., 2-n) in the dense phase fluidized bed reactor (2), and is brought into contact with a catalyst comprising SAPO-34 molecular sieve, to generate a gas phase product stream and a spent catalyst. The gas phase product stream and the entrained spent catalyst are passed into a cyclone separator (3), wherein the gas phase product stream flows through the outlet of the cyclone separator and the product material line (4) and enters into the subsequent separation section, the

10

15

20

25

30

entrained spent catalyst is passed into n<sup>th</sup> secondary reaction zone (2-n) via the dipleg of the cyclone separator; the regenerated catalyst from the dense phase fluidized bed regenerator (10) is passed into the dense phase fluidized bed reactor (2) via a stripper (13) and a lift pipe (15), wherein the bottom of the stripper (13) is connected to a water vapor line (14), and the bottom of the lift pipe (15) is connected to a lifting gas line (16); the regenerated catalyst is sequentially passed through 1<sup>st</sup> to n<sup>th</sup> secondary reaction zones (2-1, ....., 2-n) in the dense phase fluidized bed reactor (2), and forms spent catalyst after carbon deposition; the regeneration medium is introduced from regenerator feed line (9) and branch lines (9-1, ....., 9-m) thereof into secondary regeneration zones (10-1, ....., 10-m) in the dense phase fluidized bed regenerator (10), and is brought into contact with the spent catalyst, to generate exhaust gas and regenerated catalyst after charking, and then the exhaust gas and the entrained regenerated catalyst are passed into a cyclone separator (11), from which, the exhaust gas is passed into a tail gas processing section through the outlet of the cyclone separator and exhaust gas line (12), and is emitted after processing, and the entrained regenerated catalyst is passed into m<sup>th</sup> secondary regeneration zone (10-m) via the dipleg of the cyclone separator. The spent catalyst from the dense phase fluidized bed reactor (2) is passed into the dense phase fluidized bed regenerator (10) via a stripper (5) and a lift pipe (7), wherein the bottom of the stripper (5) is connected to a water vapor line (6), and the bottom of the lift pipe (7) is connected to a lifting gas line (8). In the dense phase fluidized bed regenerator (10), the spent catalyst is sequentially passed through 1st to mth secondary regeneration zones (10-1, ....., 10-m), and forms a regenerated catalyst after charking.

In a more specific embodiment, the structural schematic diagram of the dense phase fluidized bed reactor comprising 4 secondary reaction zones in the present invention is as shown in Fig. 2. Three material flow controllers (17) and one baffle are vertically provided to separate the dense phase fluidized bed

10

15

20

25

30

reaction zone into 4 secondary reaction zones. The catalyst is sequentially passed through the 1<sup>st</sup> to the 4<sup>th</sup> secondary reaction zones and is then passed into the stripper.

In a more specific embodiment, the structural schematic diagram of the dense phase fluidized bed regenerator comprising 4 secondary regeneration zones in the present invention is as shown in Fig. 3. Three material flow controllers (17) and one baffle are vertically provided to separate the regeneration zone into 4 secondary regeneration zones. The catalyst is sequentially passed through the 1<sup>st</sup> to the 4<sup>th</sup> secondary regeneration zones and is then passed into the stripper.

In a more specific embodiment, the structural schematic diagram of the stripper in the present invention is as shown in Fig. 4. The opening on the tube wall on the upper part of the stripper is a material overflow port (18) between n<sup>th</sup> secondary reaction zone (or m<sup>th</sup> secondary regeneration zone) and the stripper.

In a more specific embodiment, the structural schematic diagram of the material flow controller in the present invention is as shown in Fig. 5. The material flow controller (17) is composed of a partition plate (19), an orifice (20), a material downward flow pipe (21), a bottom baffle (22) and a heat extraction member (23). The catalyst is passed into the material downward flow pipe from the top of the downward flow pipe, wherein the apparent linear velocity of gas is less than or equals to the minimal fluidizing velocity, the catalyst in the material downward flow pipe is in a dense phase packing state, and a material flow driving force is formed to drive the catalyst to flow into a next secondary reaction zone (or regeneration zone) via the orifice. A coil structure may be used as the heat extraction member, which is fixed onto the partition plate.

Preferably, in the above technical solutions, the apparent linear velocity of gas in the dense phase fluidized bed reaction zone is 0.1-1.5 m/s; the apparent linear velocity of gas in the dense phase fluidized bed regeneration

10

15

20

25

30

zone is 0.1-1.5 m/s; the apparent linear velocity of gas in the material flow controller is less than or equals to the minimum fluidizing velocity of the catalyst; the catalyst includes SAPO-34 molecular sieve; a feed inlet is provided at the bottom of the reaction zone, and the feed includes methanol, dimethyl ether etc.; the stripping medium in the stripper includes water vapor; an inlet for regeneration medium is provided at the bottom of the regeneration zone, and the regeneration medium includes air, oxygen-deficient air, water vapor etc.; the reaction temperature in the reaction zone is 400-550 °C, the bed density is 200-1200 kg/m<sup>3</sup>, the average amount of carbon deposition on the catalyst increases sequentially from 1st to nth secondary reaction zones, the average amount of carbon deposition in the 1st secondary reaction zone is 0.5-3 wt%, the average amount of carbon deposition in the n<sup>th</sup> secondary reaction zone is 7-10 wt%; the reaction temperature in the regeneration zone is 500-700 °C, the bed density is 200-1200 kg/m<sup>3</sup>, the average amount of carbon deposition on the catalyst decreases sequentially from 1<sup>st</sup> to m<sup>th</sup> secondary regeneration zones, the average amount of carbon deposition in the 1st secondary regeneration zone is 3-10 wt%, and the average amount of carbon deposition in the m<sup>th</sup> secondary regeneration zone is 0-3 wt%. Using the method of the present invention, the object of controlling the amount of carbon deposition on catalyst, improving the uniformity of the carbon content and increasing the selectivity for light olefins can be achieved. Therefore, it has significant technical advantages, and is useful in the industrial production of light olefins.

For better illustrating the present invention, and facilitating the understanding of the technical solution of the present invention, the exemplary but non-limiting examples of the present invention are provided as follows.

#### Example 1

4 secondary reaction zones were provided in the dense phase fluidized bed reactor, and 4 secondary regeneration zones were provided in the dense

10

15

20

25

30

fluidized bed regenerator. The raw material comprising phase oxygen-containing compound was passed into the dense phase fluidized bed reactor and was brought into contact with a catalyst comprising SAPO-34 molecular sieve, to generate a gas phase product stream and a spent catalyst. The gas phase material and the entrained spent catalyst were passed into a cyclone separator. The gas phase product stream was passed into a subsequent separation section via an outlet of the cyclone separator, and the entrained spent catalyst was passed into 4<sup>th</sup> secondary reaction zone via the dipleg of the cyclone separator. The regenerated catalyst was passed into the dense phase fluidized bed reactor through a stripper and a lift pipe, and sequentially passed through 1<sup>st</sup> to 4<sup>th</sup> secondary reaction zones, forming a spent catalyst after carbon deposition. The spent catalyst was further passed into the dense phase fluidized bed regenerator through a stripper and lift pipe, and sequentially passed through 1st to 4th secondary regeneration zones, forming a regenerated catalyst after charking. The reaction conditions in the dense phase fluidized bed reactor were as follows: the reaction temperature was 400 °C, the linear velocity of gas was 0.3 m/s, the bed density was 1000 kg/m<sup>3</sup>, the average amount of carbon deposition in the 1<sup>st</sup> secondary reaction zone was 2 wt%, the average amount of carbon deposition in 2<sup>nd</sup> secondary reaction zone was 6 wt%, the average amount of carbon deposition in 3<sup>rd</sup> secondary reaction zone was 8 wt%, and the average amount of carbon deposition in 4<sup>th</sup> secondary reaction zone was 10 wt%; the reaction conditions in the dense phase fluidized bed regenerator were as follows: the reaction temperature was 500 °C, the linear velocity of gas was 0.3 m/s, the bed density was 1000 kg/m<sup>3</sup>, the average amount of carbon deposition in 1st secondary regeneration zone was 7 wt%, the average amount of carbon deposition in 2<sup>nd</sup> secondary regeneration zone was 4 wt%, the average amount of carbon deposition in 3<sup>rd</sup> secondary regeneration zone was 2 wt%, and the average amount of carbon deposition in 4<sup>th</sup> secondary regeneration zone was 1 wt%. The reaction product was analyzed by on-line gas phase chromatography, and the carbon based yield of light olefins was 91.1 wt%.

#### Example 2

5

10

15

20

25

30

3 secondary reaction zones were provided in the dense phase fluidized bed reactor, and 2 secondary regeneration zones were provided in the dense fluidized bed regenerator. The raw material comprising oxygen-containing compound was passed into the dense phase fluidized bed reactor and was brought into contact with a catalyst comprising SAPO-34 molecular sieve, to generate a gas phase product stream and a spent catalyst. The gas phase material and the entrained spent catalyst were passed into a cyclone separator, the gas phase product stream was passed into a subsequent separation section via an outlet of the cyclone separator, and the entrained spent catalyst was passed into 3<sup>rd</sup> secondary reaction zone through the dipleg of the cyclone separator. The regenerated catalyst was passed into the dense phase fluidized bed reactor through a stripper and a lift pipe, and sequentially passed through 1st to 3rd secondary reaction zones, forming a spent catalyst after carbon deposition. The spent catalyst was passed into the dense phase fluidized bed regenerator through a stripper and lift pipe, and sequentially passed through 1st to 2nd secondary regeneration zone, forming a regenerated catalyst after charking. The reaction conditions in the dense phase fluidized bed reactor were as follows: the reaction temperature was 450 °C, the linear velocity of gas was 0.5 m/s, the bed density was 900 kg/m<sup>3</sup>, the average amount of carbon deposition in 1st secondary reaction zone was 3 wt%, the average amount of carbon deposition in 2<sup>nd</sup> secondary reaction zone was 7 wt%, and the average amount of carbon deposition in 3<sup>rd</sup> secondary reaction zone was 9 wt%; the reaction conditions in the dense phase fluidized bed regenerator were as follows: the reaction temperature was 600 °C, the linear velocity of gas was 0.7 m/s, the bed density was 700 kg/m<sup>3</sup>, the average amount of carbon deposition in 1st secondary regeneration zone was 4 wt%, and the average amount of carbon deposition in 2<sup>nd</sup> secondary regeneration zone was 2 wt%. The reaction product was analyzed by on-line gas phase chromatography, and the carbon based yield of light olefins was 90.5wt%.

#### Example 3

5

10

15

20

25

30

6 secondary reaction zones were provided in the dense phase fluidized bed reactor, and 5 secondary regeneration zones were provided in the dense fluidized bed regenerator. The raw material comprising oxygen-containing compound was passed into the dense phase fluidized bed reactor, and was brought into contact with a catalyst comprising SAPO-34 molecular sieve, to generate a gas phase product stream and a spent catalyst. The gas phase material and the entrained spent catalyst were passed into a cyclone separator, the gas phase product stream was passed into a subsequent separation section via an outlet of the cyclone separator, and the entrained spent catalyst was passed into 6<sup>th</sup> secondary reaction zone via the dipleg of the cyclone separator. The regenerated catalyst was passed into the dense phase fluidized bed reactor through a stripper and a lift pipe, and sequentially passed through 1<sup>st</sup> to 6<sup>th</sup> secondary reaction zones, forming a spent catalyst after carbon deposition. The spent catalyst was further passed into the dense phase fluidized bed regenerator through a stripper and a lift pipe, and sequentially passed through 1<sup>st</sup> to 5<sup>th</sup> secondary regeneration zones, forming a regenerated catalyst after charking. The reaction conditions in the dense phase fluidized bed reactor were as follows: the reaction temperature was 480 °C, the linear velocity of gas was 0.7 m/s, the bed density was 700 kg/m<sup>3</sup>, the average amount of carbon deposition in 1st secondary reaction zone was 1 wt%, the average amount of carbon deposition in 2<sup>nd</sup> secondary reaction zone was 3 wt%, the average amount of carbon deposition in 3<sup>rd</sup> secondary reaction zone was 4 wt%, the average amount of carbon deposition in 4<sup>th</sup> secondary reaction zone was 5 wt%, the average amount of carbon deposition in 5<sup>th</sup> secondary reaction zone was 6 wt%, and the average amount of carbon deposition in 6<sup>th</sup> secondary reaction zone was 7 wt%; the reaction conditions in the dense phase

10

15

fluidized bed regenerator were as follows: the reaction temperature was 650°C, the linear velocity of gas was 1.0 m/s, the bed density was 500 kg/m³, the average amount of carbon deposition in 1<sup>st</sup> secondary regeneration zone was 5 wt%, the average amount of carbon deposition in 2<sup>nd</sup> secondary regeneration zone was 3 wt%, the average amount of carbon deposition in 3<sup>rd</sup> secondary regeneration zone was 2 wt%, the average amount of carbon deposition in 4<sup>th</sup> secondary regeneration zone was 1 wt%, and the average amount of carbon deposition in 5<sup>th</sup> secondary regeneration zone was 0.01 wt%. The reaction product was analyzed by on-line gas phase chromatography, and the carbon based yield of light olefins was 91.4wt%.

The present invention has been described in detail above, but the invention is not limited to the specific embodiments described herein. It will be appreciated by those skilled in the art that other modifications and variations can be made without departing from the scope of the invention. The scope of the invention is defined by the appended claims.

10

15

20

25

30

#### WHAT IS CLAIMED IS:

1. A method for preparing a light olefin using an oxygen-containing compound, comprising the following steps:

step a) in which a raw material comprising the oxygen-containing compound is introduced in parallel from n feeding branch lines into 1<sup>st</sup> to n<sup>th</sup> secondary reaction zones in a dense phase fluidized bed reactor, and is brought into contact with a catalyst to generate a light olefin product-containing stream and a spent catalyst, wherein said catalyst is sequentially passed through 1<sup>st</sup> to n<sup>th</sup> secondary reaction zones, with the carbon content thereof increasing gradually, and wherein said dense phase fluidized bed reactor is divided by a material flow controller into n secondary reaction zones;

step b) in which the light olefin product-containing stream flowed out from the 1<sup>st</sup> to n<sup>th</sup> secondary reaction zones is separated from the spent catalyst that it carries; said light olefin product-containing stream is passed into a product separation section, and after separation and purification, a light olefin product is obtained; the isolated spent catalyst is passed into the n<sup>th</sup> secondary reaction zone; and

step c) in which the spent catalyst flowed out from the n<sup>th</sup> secondary reaction zone, after being stripped and lifted, is passed into a dense phase fluidized bed regenerator for regeneration; said spent catalyst is sequentially passed through 1<sup>st</sup> to m<sup>th</sup> secondary regeneration zones; a regeneration medium is introduced in parallel from m feeding branch lines of regeneration zone into the 1<sup>st</sup> to m<sup>th</sup> secondary regeneration zones; the spent catalyst is brought into contact with the regeneration medium, with the carbon content thereof decreasing gradually; after the completion of the regeneration, the catalyst is returned back to the 1<sup>st</sup> secondary reaction zone via stripping and lifting; wherein the dense phase fluidized bed regenerator is divided by a material flow controller into m secondary regeneration zones;

wherein  $n \ge 2$  and  $m \ge 2$ .

10

15

20

25

30

- 2. The method according to claim 1, wherein  $8 \ge n \ge 3$  and  $8 \ge m \ge 3$ .
- 3. The method according to claim 1 or claim 2, wherein in the dense phase fluidized bed reactor, the apparent linear velocity of gas in the material flow controller is less than or equals to the minimum fluidizing velocity of the catalyst.
- 4. The method according to any one of claims 1-3, wherein in the dense phase fluidized bed regenerator, the apparent linear velocity of gas in the material flow controller is less than or equals to the minimum fluidizing velocity of the catalyst.
- 5. The method according to any one of claims 1-4, wherein the catalyst comprises SAPO-34 molecular sieve.
- 6. The method according to any one of claims 1-5, wherein the reaction conditions in the dense phase fluidized bed reaction zone are as follows: the apparent linear velocity of gas is 0.1-1.5 m/s, the reaction temperature is 400-550 °C, and the bed density is 200-1200 kg/m<sup>3</sup>.
- 7. The method according to any one of claims 1-6, wherein the average carbon deposition amount of the catalyst is increased sequentially in the 1<sup>st</sup> to n<sup>th</sup> secondary reaction zones of the dense phase fluidized bed, wherein the average carbon deposition amount of the catalyst in the 1<sup>st</sup> secondary reaction zone is 0.5-3 wt%, and the average carbon deposition amount of the catalyst in the n<sup>th</sup> secondary reaction zone is 7-10 wt%.
- 8. The method according to any one of claims 1-7, wherein the reaction conditions in the dense phase fluidized bed regeneration zone are as follows: the apparent linear velocity of gas is 0.1-1.5 m/s, the regeneration temperature is 500-700 °C, and the bed density is 200-1200 kg/m<sup>3</sup>.
- 9. The method according to any one of claims 1-8, wherein the average carbon deposition amount of the catalyst is decreased sequentially from the 1<sup>st</sup> to m<sup>th</sup> secondary regeneration zones of the dense phase fluidized bed regeneration zone, wherein the average carbon deposition amount of the catalyst in the 1<sup>st</sup> secondary regeneration zone is 3-10 wt%, and the average

10

15

carbon deposition amount of the catalyst in the m<sup>th</sup> secondary regeneration zone is 0-3 wt%.

- 10. The method according to any one of claims 1-9, wherein the oxygen-containing compound is methanol and/or dimethyl ether; the light olefin is any one of ethylene, propylene or butylene, or a mixture thereof; and the regeneration medium is any one of air, oxygen-deficient air or water vapor, or a mixture thereof.
- 11. A dense phase fluidized bed reactor used for carrying out the method according to any one of claims 1-9, said dense phase fluidized bed reactor comprising a reaction zone, a gas-solid separation zone, and a stripping zone, characterized in that the reaction zone is divided by a material flow controller into n secondary reaction zones, wherein  $n \ge 2$ .
- 12. A dense phase fluidized bed regenerator used for carrying out the method according to any one of claims 1-9, the dense phase fluidized bed regenerator comprising a regeneration zone, a gas-solid separation zone, and a stripping zone, characterized in that the regeneration zone is divided by a material flow controller into m secondary regeneration zones, wherein  $m \ge 2$ .
- 13. A product produced by the method according to any one of claims 1-10.

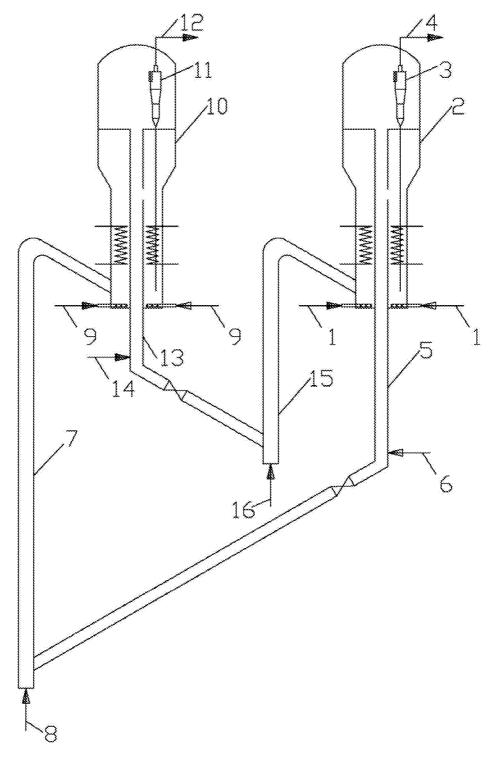
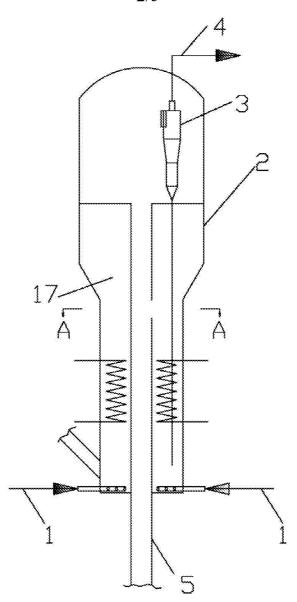


Figure 1



A-A section

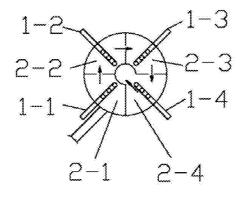
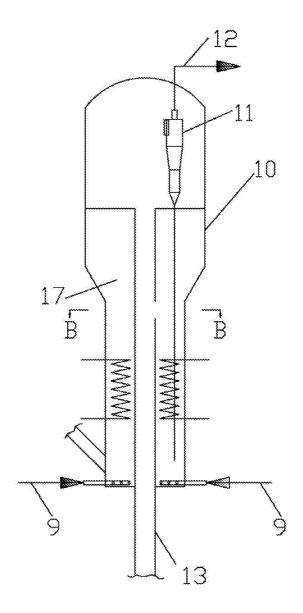


Figure 2



B-B section

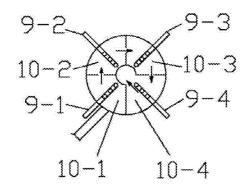
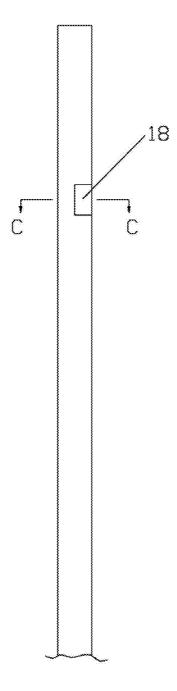


Figure 3



C-C section



Figure 4

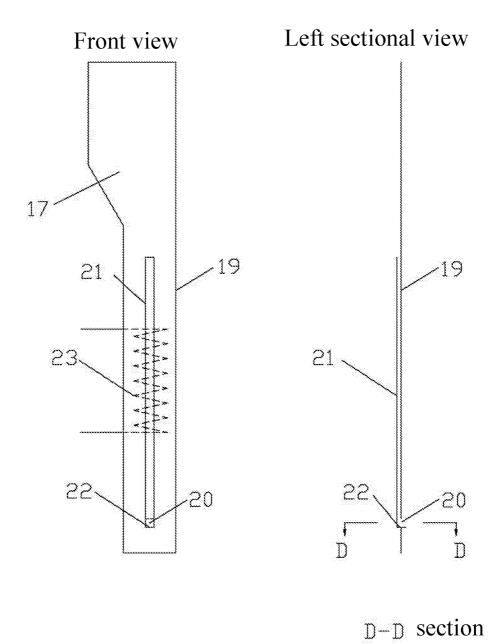


Figure 5