The efficiency and long-term stability of prior art processes may still be improved. For instance, the bed material should be fluidizable and suitable for being circulated at a very stable and high rate for an extended period of time, and without catalyzing unwanted side-reactions.

Thus, there is still a need for improving the efficiency and long term stability and industrial applicability of bed materials for thermolytic fragmentation of sugars into a composition comprising C_1-C_3 oxygenates, including glycolaldehyde.

Summary

The present inventors, having a desire to produce high purity C_1-C_3 oxygenates on an industrial scale, have found, that using the bed materials of the prior art processes for converting a sugar into glycolaldehyde and other C_1-C_3 oxygenates by thermolytic fragmentation, still has drawbacks, even though some seem to have the necessary qualities and characteristics to provide a suitable circulating fluidized bed material. When conducting the thermolytic fragmentation process in a continuous manner, the inventors found that the yield of glycolaldehyde varied significantly with time from startup of the process. They also found that the maximum yield of C_1-C_3 oxygenates had potential for improvement. In addition, they found that some materials had fluidization problems. See e.g. examples 1A to 1E.

Glycolaldehyde is an important and valuable oxygenate product (C_2 oxygenate). The inventors found that to obtain a high yield of glycolaldehyde it was important not only to obtain a high selectivity towards glycolaldehyde, but also to preserve as much as possible of the glycolaldehyde formed, i.e. by reducing further conversion of the glycolaldehyde.

The inventors have now found a bed material which is suitable for use in a circulating fluidized bed and which provides improved yields of glycolaldehyde, improved fluidization characteristics and which has improved long term stability in a thermolytic fragmentation process. For industrial application it is worth noting that even a small increase in yield, selectivity and/or conversion may result in great savings.

In an aspect of the present disclosure, there is provided a process for thermolytic fragmentation of a sugar into a composition comprising C_1-C_3 oxygenates, the process comprising:

a. Providing a circulating, fluidized stream of heat carrying particles, wherein the heat carrying particles are circulated to a heating zone to produce heated heat carrying particles, and then the heated heat carrying particles are circulated from the heating zone to a fragmentation zone to provide heat to the fragmentation zone and producing cooled heat carrying particles, and then the cooled heat carrying particles are circulated back to the heating zone for reheating.
b. introducing a feedstock solution comprising the sugar into the fragmentation zone of the circulating, fluidized stream of heat carrying particles to absorb heat and convert the sugar by thermolytic fragmentation into the C_1-C_3 oxygenates;

c. separating a fragmentation product stream comprising the C_1-C_3 oxygenates from the stream of cooled heat carrying particles; and then
d. recovering the composition comprising C_1-C_3 oxygenates from the fragmentation product stream

wherein the number of acid sites on the surface of the heat carrying particles is less than 1 µmol/g as measured by NH_3-TPD.

In another aspect of the present disclosure, there is provided a circulating fluidized bed system for fragmentation of a sugar into a composition comprising C_1-C_3 oxygenates, which system comprises a thermolytic fragmentation reactor comprising a fragmentation zone, a reheater comprising a heating zone, a first flow means arranged to transport fluidized bed material from the thermolytic fragmentation reactor to the reheater and second flow means arranged to transport fluidized bed material from the reheater to the thermolytic fragmentation reactor, and the system comprising heat carrying particles, wherein the particle surface area of the heat carrying particles is below 3 square metres per g, such as below 1, 0.5, 0.2 or 0.15 and wherein at least 90% by weight of the heat carrying particles consist of silicium, aluminium and oxygen and the mass ratio of silicium to aluminium is from 0.25 to 1.

In a further aspect of the present disclosure, there is provided a circulating fluidized bed system for fragmentation of a sugar into a composition comprising C_1-C_3 oxygenates, which system comprises a thermolytic fragmentation reactor comprising a fragmentation zone, a reheater comprising a heating zone, a first flow means arranged to transport fluidized bed material from the thermolytic fragmentation reactor to the reheater and second flow means arranged to transport fluidized bed material from the reheater to the thermolytic fragmentation reactor, and the system comprising heat carrying particles, wherein the number of acid sites on the surface of the heat carrying particles is less than 1 µmol/g as measured by NH_3-TPD, such as less than 0.5 or 0.1µmol/g.

According to an example of the present disclosure a process is provided for thermolytic fragmentation of a sugar into a composition comprising C_1-C_3 oxygenates, the process comprising:

a. Providing a circulating, fluidized stream of heat carrying particles, wherein the heat carrying particles are circulated to a heating zone to produce heated heat carrying particles, and then the heated heat carrying particles are circulated from the heating zone to a fragmentation zone to provide heat to the fragmentation zone and producing cooled heat carrying particles, and then the cooled heat carrying particles are circulated back to the heating zone for reheating.

b. introducing a feedstock solution comprising the sugar into the fragmentation zone of the circulating, fluidized stream of heat carrying particles to absorb heat and convert the sugar by thermolytic fragmentation into the C_1-C_3 oxygenates;
c. separating a fragmentation product stream comprising the C_1-C_3 oxygenates from the stream of cooled heat carrying particles; and then
d. recovering the composition comprising C_1-C_3 oxygenates from the fragmentation product stream.

In an example according to the present disclosure, the particle surface area of the heat carrying particles is below 3 square metres per g as measured by Kr physisorption, such as below 1, 0.5, 0.2 or 0.15 square metres per g. An advantage of using heat carrying particles having a surface area as low as this is that a high yield of glycolaldehyde is obtained when converting a sugar in a thermolytic fragmentation process using such heat carrying particles. Using such heat carrying particles achieves yields of glycolaldehyde above 50% and in particular when used in a continuous process.

There is not a lower limit to the surface area of the heat carrying particles below which they will not work. However, there is a natural lower limit to the surface area of the heat carrying particles depending on preparation procedure. The lower limit is the surface area where all of the particles are perfect spheres, e.g. for particles of 70 µm it is around 0.03 m^2/g. Accordingly, each of the upper limits given for the surface area may have a lower limit of e.g. 0.001 or of 0.01. Thus suitable ranges could be 3-0.001 m2/g or 1-0.01 m2/g.

In another example according to the present disclosure, at least 90% by weight of the heat carrying particles consist of silicium, aluminium and oxygen wherein the mass ratio of silicium to aluminium is from 0.25 to 1. Heat carrying particles with such composition will upon calcination at high temperatures form a large amount of mullite. Such heat carrying particles will have very low surface area (below 3 m^2/g) and a very low number of acid and basic sites and the fluidization characteristics are very suitable for use in a circulating fluidized bed reactor. Thus, the heat carrying particles may consist essentially of Al, Si and oxygen. It is to be understood that when the heat carrying particles are said to consist essentially of Al, Si and oxygen, the amount of oxygen bound in the structure is given by the amount of Aluminium (Al) and silicium (Si) respectively. However, some impurities may be present.

The amount of oxygen in the heat carrying particles is given by the amounts of silicium (Si) and aluminium (Al) present, since it will be bound with the stoichiometry of SiO_2 and Al_2O_3, respectively.

According to an example of the present disclosure, the number of acid sites on the surface of the heat carrying particles is less than 3 µmol/g as measured by NH_3-TPD, such as less than 1, 0.5, 0.1, 0.05 or 0.01 µmol/g. Acid sites on the surface of the particles could for instance be -OH groups, such as silanol groups. According to another example of the present disclosure, the number of basic sites on the surface of the heat carrying particles is less than 1 µmol/g as measured by CO2-TPD. An advantage of having a low amount of acid sites on the surface of the heat carrying particles is that the yield of glycolaldehyde is increased. Without being bound by theory, it is hypothesized that when the number of acid and/or basic sites is very low, then reactive reaction products, such as glycolaldehyde, pyruvaldehyde, glyoxal and acetol, are less prone to decompose into smaller molecules such as permanent gasses.

The process according to any of the examples of the present disclosure is suitable for continuous operation in which case the stream of heat carrying particles is a circulating stream. Such system may be referred to as a circulating fluidized bed system, wherein the heat carrying particles are continuously recirculated between a fragmentation zone and a heating zone. An advantage of continuous operation is that that the heat carrying particles have shown to provide an increasing yield of glycolaldehyde with time on stream until a steady state yield is achieved. Steady state may be achieved after 2-4 hours on stream (TOS) but it may also take longer or shorter. It will partly depend on the reactor design and operation conditions.

It is to be understood that the amount of bed material may be adjusted whenever needed by removing or adding bed material to obtain the desired amount of bed material in the circulating fluidized bed system.

In the present context, the “recovering the composition comprising C_1-C_3 oxygenates from the fragmentation product stream” is meant to refer either to collecting the fragmentation product stream as it is without further separation or to directing the same to a subsequent step, such as to a purification unit or a hydrogenation unit.

The process according to the present disclosure thus provides several advantages to achieve high glycolaldehyde selectivity and a high degree of preservation of glycolaldehyde once it has been formed. The heat carrying particles used in the process according to the present disclosure has the advantages that they have a high melting point, a very low surface area, a low number of acidic groups per weight, a low tendency to sintering during use and during calcining, a high fluidization index and a long de-aeration time. All these characteristics, provide excellent yield of glycolaldehyde and the heat carrying particles retain their excellent fluidization characteristics for an extended period of time thus making it suitable for continuous exploitation on an industrial scale. The inventors found that materials which are generally considered to be inert particles suitable for use in fluidized beds, turned out to have some catalytic effect in the thermolytic fragmentation of sugars into C_1-C_3 oxygenates. An advantage of having a very low number of acidic and/or basic groups on the surface of the heat carrying particles is that the glycolaldehyde yield is improved.

According to another example of the present disclosure a circulating fluidized bed system is provided for fragmentation of a sugar into C_1-C_3 oxygenates, which system comprises a thermolytic fragmentation reactor comprising a fragmentation zone, a reheater comprising a heating zone, a first flow means arranged to convey fluidized bed material from the thermolytic fragmentation reactor to the reheater and second flow means arranged to convey fluidized bed material from the reheater to the thermolytic fragmentation reactor, and heat carrying particles, wherein the particle surface area of the heat carrying particles is below 3 square metres per g, such as below 1, 0.5, 0.2 or 0.15 as measured by Kr physisorption, and wherein at least 90% by weight of the heat carrying particles consist of silicium, aluminium and oxygen and the mass ratio of silicium to aluminium is from 0.25 to 1.

According to another example of the present disclosure a circulating fluidized bed system is provided for fragmentation of a sugar into C_1-C_3 oxygenates, which system comprises a thermolytic fragmentation reactor comprising a fragmentation zone, a reheater comprising a heating zone, a first flow means arranged to convey fluidized bed material from the thermolytic fragmentation reactor to the reheater and second flow means arranged to convey fluidized bed material from the reheater to the thermolytic fragmentation reactor, and heat carrying particles, wherein the number of acid sites on the surface of the heat carrying particles is less than 1 µmol/g as measured by NH_3-TPD, such as less than 0.5 or 0.1µmol/g.

Such a system has the advantage of providing excellent yield of glycolaldehyde and the heat carrying particles retain their excellent fluidization characteristics for an extended period of time thus making it suitable for continuous exploitation on an industrial scale.

Figures

Fig. 1 is a sketch of the process according to the present invention.

Detailed description of the invention

Definitions

In the present context the terms “bed material” “fluidized bed material” and “heat carrying particles” are used interchangeably.

Claims

1. A process for thermolytic fragmentation of a sugar into a composition comprising C_1-C_3 oxygenates, the process comprising:
    a. Providing a circulating, fluidized stream of heat carrying particles, wherein the heat carrying particles are circulated to a heating zone to produce heated heat carrying particles, and then the heated heat carrying particles are circulated from the heating zone to a fragmentation zone to provide heat to the fragmentation zone and producing cooled heat carrying particles, and then the cooled heat carrying particles are circulated back to the heating zone for reheating.
    b. introducing a feedstock solution comprising the sugar into the fragmentation zone of the circulating, fluidized stream of heat carrying particles to absorb heat and convert the sugar by thermolytic fragmentation into the C_1-C_3 oxygenates;
    c. separating a fragmentation product stream comprising the C_1-C_3 oxygenates from the stream of cooled heat carrying particles; and then
    d. recovering the composition comprising C_1-C_3 oxygenates from the fragmentation product stream

    wherein the number of acid sites on the surface of the heat carrying particles is less than 1 µmol/g as measured by NH_3-TPD.

2. The process according to claim 1, wherein the particle surface area of the heat carrying particles is below 3 square meters per g, such as below 1, 0.5, 0.2 or 0.15.

3. The process according to claim 1 or 2, wherein at least 90% by weight of the heat carrying particles consist of silicium, aluminium and oxygen and the mass ratio of silicium to aluminium is from 0.25 to 1.

4. The process according to any one of the preceding claims, wherein the number of acid sites on the surface of the heat carrying particles is less than 0.5 µmol/g as measured by NH_3-TPD, such as less than 0.1µmol/g.

5. The process according to any one of the preceding claims, wherein the number of basic sites on the surface of the heat carrying particles is less than 1 µmol/g as measured by CO_2-TPD.

6. The process according to any one of the preceding claims, wherein the fluidization index of the heat carrying particles is above 1.

7. The process according to any one of the preceding claims, wherein 90-100%, such as 95-99.9% or 98-99.8% by weight of the heat carrying particles consist of silicium, aluminium and oxygen and the mass ratio of silicium to aluminium is of from 0.25 to 1, such as from 0.4 to 0.8 or 0.45 to 0.55.

8. The process according to any one of the preceding claims, wherein at least 50% by weight, such as at least 60%, 70%, 80%, 50-99%, 60-95% or 65-90%, of the heat carrying particles consist of mullite.

9. The process according to any one of the preceding claims, wherein the heat carrying particles have been calcined at a temperature of at least 1000 ^{O}C, such as in the range of from 1200 to 2000 ^{O}C, from 1400-1800 ^{O}C or from 1500 to 1700 ^{O}C.

10. The process according to any one of the preceding claims, wherein the heat carrying particles has a melting point above 1100 °C, such as in the range of 1100 to 3000°C.

11. The process according to any one of the preceding claims, wherein the particle density of the heat carrying particles is below 3.5 g/ml, such as in the range of from 2-3 g/ml, as measured by Hg porosimetry.

12. The process according to any one of the preceding claims, wherein the Sauter mean diameter of the heat carrying particles is from 50-150 µm.

13. The process according to any one of the preceding claims, wherein the feedstock solution comprising the sugar is fed directly into the fragmentation zone.

14. The process according to any one of the preceding claims, wherein the sugar is a mono- and/or di-saccharide.

15. The process according to any one of the preceding claims, wherein the feedstock solution comprises an aqueous solution of a sugar selected from the group consisting of sucrose, lactose, xylose, arabinose, ribose, mannose, tagatose, galactose, glucose and fructose; or mixtures thereof.

16. The process according to any one of the preceding claims, wherein the concentration of sugar in the feedstock solution is between 10 and 90% by weight.

17. The process according to any one of the preceding claims, wherein the composition comprising the C_1-C_3 oxygenates comprises one or more of glycolaldehyde, glyoxal, pyruvaldehyde, acetol and formaldehyde.

18. The process according to any one of the preceding claims, wherein the fragmentation zone has a fragmentation temperature in the range of from 250 - 900 °C, such as from 300-750, 350-650, or 400-550 °C.

19. The process according to any one of the preceding claims, wherein the heated heat carrying particles have a temperature in the range of from 300-950 °C, such as from 350-800, 400-700 or 450-650 °C as measured when the heated heat carrying particles leave the heating zone.

20. The process according to any one of the preceding claims, wherein the cooled heat carrying particles have a temperature in the range of from 200-850 °C, such as from 250-700, 300-600, or 350-550 °C as measured when the cooled heat carrying particles leave the fragmentation zone.

21. The process according to any one of the preceding claims, wherein the fragmentation zone is delimited by a riser suitable for conducting thermolytic fragmentation of a feedstock solution comprising a sugar and suitable for fluidizing the stream of heat carrying particles.

22. The process according to any one of the preceding claims, wherein the heating zone is delimited by a riser suitable for heating and suitable for fluidizing the stream of heat carrying particles.

23. The process according to any one of the preceding claims, wherein the fragmentation product stream is separated from the stream of cooled heat carrying particles by inertial separation.

24. The process according to any one of the preceding claims, wherein the composition comprising the C_1-C_3 oxygenates is recovered by quench cooling of the fragmentation product stream.

25. The process according to any one of the preceding claims, wherein the ratio of the mass flow rate of heat carrying particles per mass flow rate of feedstock is between 12:1 and 200:1.

26. The process according to any one of the preceding claims, wherein step d) of recovering the composition comprising C_1-C_3 oxygenates comprises collecting the fragmentation product stream and conveying it to a hydrogenation unit to convert the C_1-C_3 oxygenates into the corresponding poly-alcohols.

27. A circulating fluidized bed system for fragmentation of a sugar into a composition comprising C_1-C_3 oxygenates, which system comprises a thermolytic fragmentation reactor comprising a fragmentation zone, a reheater comprising a heating zone, a first flow means arranged to transport fluidized bed material from the thermolytic fragmentation reactor to the reheater and second flow means arranged to transport fluidized bed material from the reheater to the thermolytic fragmentation reactor, and the system comprising heat carrying particles, wherein the particle surface area of the heat carrying particles is below 3 square metres per g, such as below 1, 0.5, 0.2 or 0.15 and wherein at least 90% by weight of the heat carrying particles consist of silicium, aluminium and oxygen and the mass ratio of silicium to aluminium is from 0.25 to 1.

28. A circulating fluidized bed system for fragmentation of a sugar into a composition comprising C_1-C_3 oxygenates, which system comprises a thermolytic fragmentation reactor comprising a fragmentation zone, a reheater comprising a heating zone, a first flow means arranged to transport fluidized bed material from the thermolytic fragmentation reactor to the reheater and second flow means arranged to transport fluidized bed material from the reheater to the thermolytic fragmentation reactor, and the system comprising heat carrying particles, wherein the number of acid sites on the surface of the heat carrying particles is less than 1 µmol/g as measured by NH_3-TPD, such as less than 0.5 or 0.1µmol/g.

29. The circulating fluidized bed system according to claim 28, wherein the particle surface area of the heat carrying particles is below 3 square metres per g, such as below 1, 0.5, 0.2 or 0.15 square meters per g.