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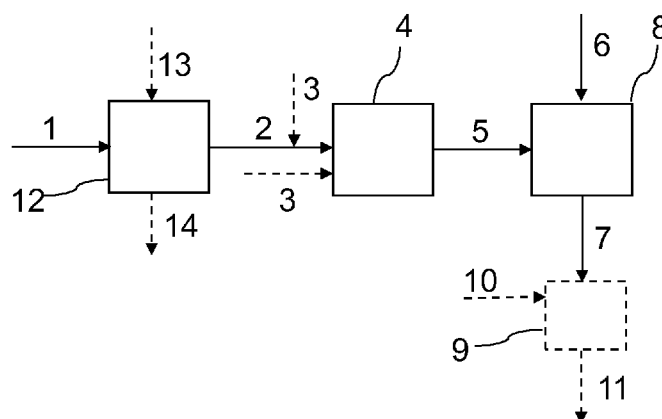


Fig. 1

(57) Abstract: The invention relates to a method and an apparatus for producing a formate or formic acid from carbon dioxide. A bicarbonate solution (5) comprising at least bicarbonate is formed from a mixture (2) which comprises at least carbon dioxide and which further comprises carbonate, ammonia and/or hydroxide (3), and the bicarbonate solution (5) is treated by a reaction with a metal catalyst in a reactor (8), in which hydrogen and/or carbon monoxide (6) is supplied to the reactor and temperature is 10 - 70 °C and pressure is 1 - 100 bar during the reaction, in order to produce the formate (7), and optionally the formic acid (11) is produced from the formate. Further, the invention relates to the use of the method.



## METHOD AND APPARATUS FOR PRODUCING FORMATE OR FORMIC ACID FROM CARBON DIOXIDE AND USE

### FIELD

5           The application relates to a method defined in claim 1 and an apparatus defined in claim 14 for producing a formate or formic acid from carbon dioxide. Further, the application relates to a use of the method defined in claim 16.

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### BACKGROUND

          Known from the prior art is to produce different formates and formic acids by means of different methods, typically from fossil raw materials.

15           The formic acid may be produced from synthesis gas such that firstly methyl formate is formed and after that the formic acid is formed from the methyl formate. The main problems are associated with work-up of hydrolysis mixtures. Because of the unfavorable position of the equilibrium, reesterification of the methanol and formic acid to the methyl formate occurs rapidly during a separation of unreacted methyl formate. Problems also arise in the selection of sufficiently corrosion-resistant materials.

20           Further, a formic acid production from carbon dioxide has been demonstrated in laboratory scale. However, the formic acid production from carbon dioxide requires a complex and expensive catalytic system which is difficult to scale up, and separation of catalysts and solvents requires a lot of energy.

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### OBJECTIVE

          The objective is to solve the above problems. Further, the objective is to disclose a new type of method and apparatus for producing a formate or formic acid. Further, the objective is to disclose a simple method for producing the formate or formic acid from

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carbon dioxide. Further, the objective is to utilize a captured carbon dioxide for producing the formate or formic acid.

## 5 SUMMARY

The method and apparatus and use are characterized by what are presented in the claims.

In the method and apparatus, a bicarbonate solution comprising at least bicarbonate is formed from a mixture which comprises at least carbon dioxide and the bicarbonate solution is treated by a reaction with a metal catalyst in a reactor in order to produce a formate, and optionally to produce a formic acid from the formate.

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## BRIEF DESCRIPTION OF THE DRAWING

The accompanying drawing, which is included to provide a further understanding of the invention and constitutes a part of this specification, illustrates some embodiments of the invention and together with the description help to explain the principles of the invention. In the drawing:

Fig. 1 is a flow chart illustration of a process according to one embodiment.

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## DETAILED DESCRIPTION

In a method for producing a formate or formic acid from carbon dioxide, the method comprises: forming a bicarbonate solution (5) comprising at least bicarbonate from a mixture (2) which comprises at least carbon dioxide and which further comprises carbonate, ammonia and/or hydroxide (3), and treating the bicarbonate solution (5) by a reaction with a metal catalyst in a reactor (8), in which hydrogen and/or carbon monoxide (6) is supplied to the reactor and temperature is 10 - 70 °C and pressure is 1 - 100 bar during the reaction, in order to produce the formate (7). Op-

tionally the formic acid (11) can be produced from the formate.

An apparatus for producing a formate or formic acid from carbon dioxide, wherein the apparatus  
5 comprises at least one equipment (4) into which a mixture (2) which comprises at least carbon dioxide and which further comprises carbonate, ammonia and/or hydroxide (3) is subjected for forming a bicarbonate solution (5) comprising at least bicarbonate, and at  
10 least one reactor (8) in which the bicarbonate solution is treated by a reaction with a metal catalyst at temperature of 10 - 70 °C and pressure of 1 - 100 bar and at least one feeding device for supplying the hydrogen and/or carbon monoxide (6) into the reactor in  
15 order to produce the formate (7). Optionally the formic acid (11) can be produced from the formate.

Some embodiments of the method and the apparatus are shown in Fig. 1.

In this context, the bicarbonate solution (5)  
20 means any solution, which contains at least bicarbonate and solvent, e.g. water, ethanol, other solvent or their combinations. The bicarbonate solution is CO<sub>2</sub>-derived carbonate solution. In one embodiment, the solvent of the bicarbonate solution comprises water  
25 and ethanol. The bicarbonate solution can comprise also other components than the bicarbonate and the solvent. The bicarbonate solution can comprise one or more components. In one embodiment, the bicarbonate solution comprises at least bicarbonate and/or carbonate. In one embodiment, the bicarbonate is formed  
30 in the mixture comprising at least carbon dioxide, such as a captured CO<sub>2</sub>, and further carbonate, ammonia and/or hydroxide. In one embodiment, the carbonate is selected from sodium carbonate, ammonium carbonate, potassium carbonate, magnesium carbonate or their combinations. In one embodiment, the bicarbonate is sodi-  
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um bicarbonate, ammonium bicarbonate, potassium bicarbonate, magnesium bicarbonate or their combinations.

In this context, the mixture (2) means any mixture comprising at least carbon dioxide, such as a captured carbon dioxide. The mixture is in a liquid form, e.g. solution, aqueous solution or the like. In one embodiment, the mixture comprises water, i.e. the carbon dioxide is in an aqueous solution. Further, the mixture comprises carbonate, ammonia and/or hydroxide. The mixture can comprise also other components. The mixture can comprise one or more components. In one embodiment, the carbonate is selected from sodium carbonate, ammonium carbonate, potassium carbonate, magnesium carbonate or their combinations. The mixture may comprise carbonate, ammonia and/or hydroxide, or carbonate, ammonia and/or hydroxide may be added to the mixture.

In this context, the formate (7) means any formate, formate salt, formate product or the like which is formed from the bicarbonate solution comprising the bicarbonate.

In this context, the formic acid (11) means any formic acid, formic acid product or the like which is formed from the bicarbonate solution comprising the bicarbonate and/or from the formate.

In one embodiment, the carbon dioxide is captured and the mixture (2) is formed. In one embodiment, the mixture may comprise carbonate, ammonia and/or hydroxide, or carbonate, ammonia and/or hydroxide may be added to the mixture. In one embodiment, the carbon dioxide is captured into a solution. In one embodiment, the carbon dioxide is captured directly into the mixture. In one embodiment, the carbon dioxide is captured, a blend or stream comprising the carbon dioxide is formed, and the mixture (2) is formed from said blend or stream. In one embodiment, the carbon dioxide is captured, a blend or stream comprising

the carbon dioxide is formed, at least one fraction or phase is separated from said blend or stream and the mixture (2) is formed from said fraction or phase. In one embodiment, the blend or stream or their fraction  
5 may comprise carbonate, ammonia and/or hydroxide, or carbonate, ammonia and/or hydroxide may be added to the the blend or stream or their fraction or to the mixture which is formed. In one embodiment, the carbon dioxide is captured from a gas (1) which comprises  
10 carbon dioxide, e.g. from raw gas, biomass derived gas, biogas, gas from biomass pyrolysis, synthesis gas, exhaust gas, flue gas, hydrogen containing gas, gasification gas, fermentation gas, gas from biomass treating process, gas from black liquor process or the  
15 like or their combinations. In one embodiment, the carbon dioxide is captured from a liquid which comprises carbon dioxide. The carbon dioxide may be captured by means of any suitable method or device (12), e.g. capture device, ejector or the like, from the gas  
20 or liquid. In one embodiment, the apparatus comprises at least one capture device or ejector for capturing the carbon dioxide.

In one embodiment, the carbon dioxide is captured from a gas into a solution, such as into the  
25 mixture (2). In one embodiment, the gas comprising carbon dioxide is treated in a treatment comprising at least one capture device, e.g. a column, and the carbon dioxide is captured from the gas into the solution in the treatment. Any suitable device can be used to  
30 capture the carbon dioxide. In one embodiment, the solution comprises the carbonate, ammonia and/or hydroxide. In one embodiment, the carbonate, ammonia and/or hydroxide may be added in connection with the capture of the carbon dioxide for forming the mixture. In one  
35 embodiment, the carbonate, ammonia and/or hydroxide may be added later into the mixture. In one embodiment, at least one fraction or phase is separated af-

ter the capturing, e.g. a gas phase is separated from a liquid phase and the mixture is formed from the liquid phase. In one embodiment, the apparatus comprises at least one separation device for separating desired phases or fractions. The mixture may be formed from a predetermined phase or fraction.

In one embodiment, the gas comprising carbon dioxide is treated in a treatment comprising at least one ejector stage wherein a motive medium, e.g. at high pressure, is injected to at least one ejector of the ejector stage and the gas is sucked into the same ejector in which the gas is mixed with the motive medium for forming a blend of the gas and motive medium. Then the carbon dioxide is captured into the blend. In one embodiment, the blend of the gas and motive medium is used as the mixture or the mixture which comprises CO<sub>2</sub> is separated, e.g. as a liquid phase, from the blend of the gas and motive medium. In one embodiment, the gas (1) comprising carbon dioxide is treated in at least one ejector stage for capturing the carbon dioxide wherein a motive medium is injected to at least one ejector of the ejector stage and the gas is sucked into the same ejector in which the gas is mixed with the motive medium for forming a blend of the gas and motive medium, and the mixture is formed from the blend of the gas and motive medium or from a liquid phase of the blend. Preferably, the liquid phase is a carbon dioxide rich phase. In one embodiment, the method and apparatus may comprise more than one ejector stages. In one embodiment, gas and liquid phases may be separated after the ejector stage. In one embodiment, the apparatus comprises at least one separation device for separating the gas and liquid phases. In one embodiment, the carbon dioxide can be captured from the gases comprising CO<sub>2</sub> by means of the method or apparatus presented in patent application WO 2018206850. In one embodiment, the carbonate, ammonia

and/or hydroxide is added to the blend or the mixture, or the blend or the mixture comprises the carbonate, ammonia and/or hydroxide. In one embodiment, the carbonate, ammonia and/or hydroxide is added in connection with the ejector stage, or before the ejector stage, or after the ejector stage. In one embodiment, the carbonate, ammonia and/or hydroxide is added to the liquid phase or to the mixture after the separation.

10 In one embodiment, the mixture (2) comprises the carbonate, ammonia and/or hydroxide. In one embodiment, the CO<sub>2</sub>-containing stream from the capture is subjected to the mixture comprising the carbonate, ammonia and/or hydroxide. In one embodiment, the CO<sub>2</sub> is  
15 captured into the mixture comprising the carbonate, ammonia and/or hydroxide. In one embodiment, a blend or stream comprising the carbon dioxide comprises the carbonate, ammonia and/or hydroxide, and the mixture is formed from the blend or stream or from a fraction or phase of the blend or stream. In one embodiment, the predetermined carbonate, ammonia and/or hydroxide  
20 (3) is added to the mixture. In one embodiment, the predetermined carbonate, ammonia and/or hydroxide is added to the blend or stream comprising the carbon dioxide in connection with the capture of the carbon dioxide or after the capture, or to the phase or fraction separated from the blend or stream. In one embodiment, the predetermined carbonate, ammonia and/or hydroxide is added in one or more steps.

30 In one embodiment, the mixture (2) and its components, such as CO<sub>2</sub> and further carbonate, ammonia and/or hydroxide are given to react in a solution, such as an aqueous solution, in order to form bicarbonates. In one embodiment, CO<sub>2</sub> and carbonate, ammonia  
35 and/or hydroxide are given to react in the mixture for forming bicarbonates. In one embodiment, the bicarbonate is formed in the mixture. In one embodiment,

the bicarbonate is formed in connection with the capturing or after the capture of the carbon dioxide. In one embodiment, the bicarbonate is formed in connection with the separation. In one embodiment, the bicarbonate is formed after the capture of the carbon dioxide and the separation.

The formation of the bicarbonates may be carried out in any suitable equipment (4) or device. In one embodiment, the equipment (4) in which the bicarbonate is formed may be any treatment device, reactor, mixer, vessel, pipe, other suitable equipment, or their combinations.

In one embodiment, the bicarbonate solution (5) is formed from the mixture (2). In one embodiment, the bicarbonate solution (5) is formed directly from the mixture. In one embodiment, the bicarbonate solution (5) is formed by separating or recovering the bicarbonates from the mixture and by forming the bicarbonate solution from the bicarbonates. In one embodiment, the bicarbonate solution (5) is the mixture (2).

In one embodiment, the bicarbonate solution (5) is formed directly from the mixture (2) comprising the captured carbon dioxide, without a purification of the mixture. The mixture or the bicarbonate solution may comprise impurities, e.g.  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{NH}_3$ ,  $\text{HCl}$ ,  $\text{SO}_4^{2-}$  and/or  $\text{Cl}^-$ . By means of the process of the invention  $\text{CO}_2$ -containing gases which comprise impurities can be converted into the formates and formic acids.

The hydrogen and/or carbon monoxide (6) is supplied to the reactor (8). In one embodiment, at least hydrogen is supplied to the reactor. In one embodiment, at least carbon monoxide is supplied to the reactor. In one embodiment, synthesis gas is supplied to the reactor. In one embodiment, gas comprising carbon monoxide is supplied to the reactor. In one embodiment, gas comprising carbon monoxide and hydrogen is supplied to the reactor. In one embodiment, hydrogen,

carbon monoxide, synthesis gas, gas comprising carbon monoxide and/or gas comprising carbon monoxide and hydrogen is supplied to the reactor. In one embodiment, the apparatus comprises at least one feeding device  
5 for supplying the hydrogen, carbon monoxide, synthesis gas, gas comprising carbon monoxide and/or gas comprising carbon monoxide and hydrogen into the reactor. Hydrogen containing gases, e.g. unused hydrogen from industrial sites, and/or carbon monoxide containing  
10 gases, e.g. from coke ovens, pyrolysis or gasification, may be used as raw materials to hydrogenate bicarbonates into the formates in the reactor. In one embodiment, the hydrogen may be fed in connection with a capture of the carbon dioxide, e.g. to a first or  
15 second ejector in which the gas comprising carbon dioxide is treated, or after the capture, and then the mixture (2) further comprises the hydrogen.

In the reactor (8), the bicarbonate solution (5) is treated to form the formate (7), i.e. the bicarbonate solution is hydrogenated into the corresponding formate with the metal catalyst.  
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In one embodiment, temperature is 15 - 50 °C, in one embodiment 20 - 45 °C, during the reaction in the reactor (8). In one embodiment, pressure is 20 -  
25 60 bar, in one embodiment 30 - 50 bar, during the reaction in the reactor (8). In one embodiment, reaction time is 0.5 - 2 hours, in one embodiment about 1 hour, in the reactor. In one embodiment, pressure of the hydrogen is 20 - 40 bar, in one embodiment about 30 bar.  
30 Preferably, the reaction is performed in presence of the hydrogen and/carbon monoxide in the reactor. In one embodiment, the reaction is performed in presence of at least the hydrogen in the reactor.

In one embodiment, any suitable metal catalyst may be used in the reactor. In one embodiment,  
35 the catalyst comprises precious metal, such as Pd, Pt, Ru, Au or other suitable precious metal. In one embod-

iment, the catalyst comprises a carrier material, and the carrier material of the catalyst comprises activated carbon,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{ZrO}_2$ ,  $\text{MgO}$ ,  $\text{SiO}_2$ ,  $\text{CeO}_2$ ,  $\text{CeZrO}_x$  or other suitable carrier material. In one embodiment, the reactor comprises a catalyst bed or at least one catalyst element. In one embodiment, the catalyst bed of the reactor comprises at least the metal catalyst. The catalyst bed may further comprise bed material, e.g. sand. Any suitable bed material may be used. In one embodiment, the catalyst element comprises at least the metal catalyst.

The reactor (8) may be any reactor, device or pressurized vessel or the like in which the formate (7) can be produced under heating and pressure. In one embodiment, the reactor is a fixed bed reactor, trickle bed reactor, loop reactor or the like.

In one embodiment, the formate (7) can be used as such or can be treated, post-treated or supplied to a next process or a next process step after the reactor (8). In one embodiment, the formate is recovered after the reactor. In one embodiment, the formate is treated to form the formic acid (11).

In one embodiment, the formic acid (11) is produced. In one embodiment, a strong acid (10), e.g. phosphoric acid,  $\text{HCl}$  or sulphuric acid, is added to the formate, and the formate is treated, e.g. by decomposing, in order to form the formic acid. In one embodiment, the phosphoric acid is added to the formate, and the formate is treated by decomposing in order to form the formic acid and phosphate salt. In one embodiment, a formed salt product, e.g. ammonium phosphate or magnesium chloride, produced as a by-product in the production of the formic acid is decomposed by a heat treatment or by heating, e.g. at  $200^\circ\text{C}$ , back to a strong acid, e.g. molten phosphoric acid or  $\text{HCl}$ , and to a base, e.g. ammonia or magnesium compound. The formed salt product which is produced as a by-product

in the production of the formic acid may be, for example, ammonium phosphate, sodium phosphate, potassium phosphate or magnesium chloride. In one embodiment, the formed strong acid, e.g. phosphoric acid or HCl, can be recycled to the production of the formic acid in which the formate is decomposed into the formic acid. In one embodiment, the formed ammonia may be recycled to the capture of the carbon dioxide or to the mixture. In one embodiment, sulphuric acid is used as the strong acid in the production of the formic acid, and the spent sulphuric acid containing sulphates can be regenerated in a process where the sulphates are thermally decomposed into  $\text{SO}_2$ , and the sulphuric acid is produced back from  $\text{SO}_2$ . In the formate and formic acid production, the acids and bases may be recycled, and waste salt production can be avoided. The formic acid may be produced in any reactor, device, vessel or the like.

In one embodiment, methyl formate or ethyl formate is produced. In one embodiment, methyl formate or ethyl formate is formed from a formed formate or a formic acid. In one embodiment, methanol or ethanol is produced. In one embodiment, formic acid and methanol is formed from the methyl formate.

In one embodiment, methyl formate or methanol is produced. In one embodiment, the methyl formate is formed by converting a formed formate, e.g. ammonium formate, into a formic acid in a solution comprising methanol by adding a small amount of strong acid, e.g. sulphuric acid that catalyses a reaction of the formed acid and methanol into the methyl formate. The methyl formate can be separated, for example by a reactive distillation, evaporation or the like method. The methanol can be formed by hydrogenation of the methyl formate. Instead of methanol ethanol can be used to produce ethyl formate.

In one embodiment, the formate is decomposed into hydrogen or into hydrogen and CO<sub>2</sub>. In one embodiment, the formate, e.g. ammonium formate, is decomposed into hydrogen and CO<sub>2</sub>, and further for example ammonium bicarbonate and/or ammonium carbonate, at elevated temperatures, and optionally by using metal catalyst, and the remaining liquid may be returned to the reactor. In one embodiment, the formate solution can be used as a storage medium for both hydrogen and CO<sub>2</sub>. The formed mixture of CO<sub>2</sub> and hydrogen can be further converted to a product, such as to fuel or chemicals, thereby storing renewable electricity according to Power to X concepts.

In one embodiment, the formate product can be used as a hydrogen donor in transfer hydrogenation where a substance, such as biocrude, liquid organic hydrogen carrier etc., is hydrogenated directly with the hydrogen donor under mild process conditions instead of employing hydrogen gas at high pressure and temperature.

In one embodiment, the formate (7) is formed at one or more process stages. In one embodiment, the carbon dioxide is captured in more than one capture steps. In one embodiment, the formic acid (11) is formed in more than one reaction steps and reactors. The capture steps or reaction steps may be sequential process steps or parallel process steps.

In one embodiment, the method and apparatus are based on a continuous process.

In one embodiment, the method and apparatus can be used in a production of formate, e.g. sodium formate, ammonium formate, potassium formate or magnesium formate, in a production of formic acid, in a treatment of captured carbon dioxide, in a production of a chemical or liquid for using as a carrier of carbon dioxide and/or hydrogen, in a production of methanol, or their combinations. In one embodiment, the

liquid is used as the carrier of carbon dioxide and/or hydrogen for storing energy from renewable power production, production of methyl and ethyl, production of formate or production of methanol.

5           Thanks to the invention, a simple process is provided to produce different formates and formic acids from the carbon dioxide based raw material, e.g. from CO<sub>2</sub>-containing gases. For example, industrial sources which comprise carbon dioxide can be used as  
10 raw material for producing the formates and formic acids. Further, a production of waste salts can be avoided or prevented in this process.

          The method and apparatus offer a possibility to produce the formates and formic acids with good  
15 properties easily, and energy- and cost-effectively. The present invention provides an industrially applicable, simple and affordable way to produce the desired formate and formic acid products. The method and apparatus are easy and simple to realize in connection  
20 with production processes.

#### **EXAMPLES**

          Fig. 1 presents some embodiments of the process for producing formate from CO<sub>2</sub>-containing mixture  
25 and formic acid from the formate.

          The apparatus comprises at least one equipment (4) into which a mixture (2) which comprises at least carbon dioxide and which further comprises carbonate, ammonia and/or hydroxide (3) is subjected for  
30 forming a bicarbonate solution (5) comprising at least bicarbonate. The bicarbonate solution (5) may comprise also carbonate. The carbon dioxide is captured from a gas comprising CO<sub>2</sub> (1) in a capture stage (12) comprising a capture device of the carbon dioxide. If the  
35 capture device is an ejector, a motive medium (13) can be fed to the ejector. The capture stage (12) may comprise a separation device for separating a purified

gas (14) from the mixture (2) comprising at least the carbon dioxide. The mixture (2) may comprise carbonate, ammonia and/or hydroxide, or carbonate, ammonia and/or hydroxide (3) are added to the mixture before the equipment (4) or in the equipment. The bicarbonate solution (5) comprising at least bicarbonate, and in one embodiment also carbonate, is formed in the equipment which may be, for example, a pipe, vessel or mixer and in which the components of the mixture react to form the bicarbonates.

Further, the apparatus comprises at least one reactor (8). At least one feeding device is arranged to supply the hydrogen and/or carbon monoxide (6) into the reactor (8). The bicarbonate solution (5) is treated by a reaction with a metal catalyst at temperature of 10 - 70 °C, in one embodiment 15 - 50 °C, and pressure of 1 - 100 bar in the reactor, and the formate (7) is formed.

The formic acid (11) may be produced from the formate (7). The formate (7) is fed to a formic acid reactor (9). Further, a strong acid (10), e.g. phosphoric acid or HCl or sulphuric acid, is supplied to the formic acid reactor (9), and the formic acid (11) is formed from the formate.

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#### Example 1

In this example, the production of the sodium formate and the formic acid is performed according to the apparatus of Fig. 1.

CO<sub>2</sub> is captured and mixed with sodium carbonate to form a mixture which is an aqueous solution. In the mixture CO<sub>2</sub> reacts with the sodium carbonate to form sodium bicarbonate, and a bicarbonate solution comprising the sodium bicarbonate is formed. The bicarbonate solution is supplied to a reactor. Further, hydrogen is supplied to the reactor. In the reactor, the bicarbonate solution is hydrogenated with a metal

catalyst at temperature of 20 - 50 °C and in pressure of 30 - 60 bar for forming the sodium formate.

Further, the formic acid is formed from the sodium formate. A phosphoric acid is added to the sodium formate, and the sodium formate is treated with the phosphoric acid by decomposing the sodium formate to the formic acid and sodium phosphate.

#### Example 2

In this example, the production of the ammonium formate and the formic acid is performed according to the apparatus of Fig. 1.

CO<sub>2</sub> is captured and mixed with ammonium carbonate to form a mixture which is an aqueous solution. In the mixture CO<sub>2</sub> reacts with the ammonium carbonate to form ammonium bicarbonate, and a bicarbonate solution comprising the ammonium bicarbonate is formed. The bicarbonate solution is supplied to a reactor. Further, hydrogen is supplied to the reactor. In the reactor, the bicarbonate solution is hydrogenated with a metal catalyst at temperature of 20 - 50 °C and in pressure of 30 - 60 bar for forming the ammonium formate.

Further, the formic acid is formed from the ammonium formate. A phosphoric acid is added to the ammonium formate, and the ammonium formate is treated with the phosphoric acid by decomposing the ammonium formate to the formic acid and ammonium phosphate. The ammonium phosphate may be decomposed back to gaseous ammonia and molten phosphoric acid. The phosphoric acid may be recycled to the production of the formic acid. The ammonia may be recycled to the capture of the carbon dioxide or to the mixture.

#### Example 3

In this example, the continuous production of the ammonium formate was examined.

Ammonium bicarbonate was formed from CO<sub>2</sub>, and a bicarbonate solution comprising the ammonium bicarbonate was formed. The bicarbonate solution included water + 1 M ammonium bicarbonate (50 wt%) and ethanol (50 wt%). The bicarbonate solution was supplied to a reactor, and liquid feed was 0.09 ml/min. Further, hydrogen, 50 ml/min, was supplied to the reactor. In the reactor, the bicarbonate solution was hydrogenated with 1.1 g Pd/AC (5 wt%) catalyst, in which AC is activated carbon, at temperature of about 21 °C and in pressure of 30 bar for forming the ammonium formate.

It was observed from the test that yields of the ammonium formate were similar, about 30 - 42 %, in relation to time during the continuous process.

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#### Example 4

In this example, the bicarbonate solution and formate were formed.

Carbon dioxide was captured and absorbed into an aqueous solution which comprised ammonium carbonate. In the solution the carbon dioxide reacted with the ammonium carbonate to form ammonium bicarbonate. Then the bicarbonate solution was formed, and the bicarbonate solution comprised ammonium bicarbonate and ammonium carbonate. The ammonium formate was formed from the bicarbonate solution.

#### Example 5

In this example, the carbonate and bicarbonate were compared in the production of the formate. The carbonate was ammonium carbonate, and the bicarbonate was ammonium bicarbonate.

Carbonate solutions comprising the ammonium carbonate or ammonium bicarbonate were fed to a reactor which has 2 g Pd/AC (1 wt%) -catalyst, in which AC is activated carbon. The reactions were performed in

the reactor. The pressure of hydrogen was 30 bar and temperature was about 20 °C in the reactor.

It was observed from this test that yield of the formate was 16.1 %, when the carbonate solution comprising the ammonium carbonate was used, and 31.6 %, when the carbonate solution comprising the ammonium bicarbonate was used.

#### Example 6

In this example, the bicarbonates were compared in the production of the formate. The bicarbonates were ammonium bicarbonate, sodium bicarbonate and potassium bicarbonate.

The reactions were performed as batch experiments in 50 ml autoclave. Reaction time was 1 h. The pressure of hydrogen was 30 bar in the autoclave. 1 M bicarbonate solution in H<sub>2</sub>O was fed to the autoclave which has 0.1 g Pd/AC -catalyst, in which AC is activated carbon.

It was observed from this test that yield of the formate was best, about 50 %, when potassium bicarbonate was used.

#### Example 7

In this example, the solvents of the bicarbonate solutions were compared in the production of the ammonium formate.

The bicarbonate solutions included ammonium bicarbonate. The bicarbonate solution A included 20 ml H<sub>2</sub>O and the ammonium bicarbonate. The bicarbonate solution B included 15 ml H<sub>2</sub>O + 10 ml ethanol and the ammonium bicarbonate. The bicarbonate solutions were fed to a reactor which has Pd(5 wt%)/AC -catalyst, in which AC is activated carbon. Reaction time was 1 h. The pressure of hydrogen was 30 bar and temperature was 20 °C in the reactor.

It was observed from this test that yield of the ammonium formate was 30.4 %, when the bicarbonate solution A comprising H<sub>2</sub>O was used, and 49.3 %, when the bicarbonate solution B comprising H<sub>2</sub>O and ethanol  
5 was used.

The reactor and other devices and equipments of the process used in Fig. 1 are known per se in the art, and therefore they are not described in any more  
10 detail in this context.

The method and apparatus are suitable in different embodiments for producing formates and formic acids from different CO<sub>2</sub> based raw materials.

The invention is not limited merely to the  
15 examples referred to above; instead many variations are possible within the scope of the inventive idea defined by the claims.

**CLAIMS**

1. A method for producing a formate or formic acid from carbon dioxide, characterized in that the method comprises

- 5       - forming a bicarbonate solution (5) comprising at least bicarbonate from a mixture (2) which comprises at least carbon dioxide and which further comprises carbonate, ammonia and/or hydroxide (3), and
- 10       - treating the bicarbonate solution (5) by a reaction with a metal catalyst in a reactor (8), in which hydrogen and/or carbon monoxide (6) is supplied to the reactor and temperature is 10 - 70 °C and pressure is 1 - 100 bar during the reaction,
- 15       in order to produce the formate (7), and optionally producing the formic acid (11) from the formate.

2. The method according to claim 1, characterized in that the bicarbonate solution (5)

20 contains the bicarbonate and a solvent.

3. The method according to claim 2, characterized in that the solvent of the bicarbonate solution (5) comprises water and ethanol.

4. The method according to any one of claims

25 1 to 3, characterized in that the carbon dioxide is captured, and the mixture (2) is formed.

5. The method according to any one of claims 1 to 4, characterized in that the carbon dioxide is captured from a gas (1) which comprises carbon

30 dioxide.

6. The method according to any one of claims 1 to 5, characterized in that the gas (1) comprising carbon dioxide is treated in at least one ejector stage for capturing the carbon dioxide wherein

35 a motive medium is injected to at least one ejector of the ejector stage and the gas (1) is sucked into the same ejector in which the gas is mixed with the motive

medium for forming a blend of the gas and motive medium, and the mixture (2) is formed from the blend of the gas and motive medium or from a liquid phase of the blend.

5               7. The method according to any one of claims 1 to 6, characterized in that the carbonate, ammonia and/or hydroxide is added to the mixture (2).

              8. The method according to any one of claims 1 to 7, characterized in that hydrogen, carbon monoxide, synthesis gas, gas comprising carbon monoxide and/or gas comprising carbon monoxide and hydrogen is supplied to the reactor (8).

              9. The method according to any one of claims 1 to 8, characterized in that temperature is 15   15 - 50 °C during the reaction in the reactor (8).

              10. The method according to any one of claims 1 to 9, characterized in that pressure is 20 - 60 bar during the reaction in the reactor (8).

              11. The method according to any one of claims 20 1 to 10, characterized in that a strong acid (10) is added to the formate (7), and the formate is treated in order to form the formic acid (11).

              12. The method according to claim 11, characterized in that a formed salt product 25 produced as a by-product in the production of the formic acid (11) is decomposed by a heat treatment or by heating back to a strong acid (10).

              13. The method according to claim 12, characterized in that the formed strong acid 30 is recycled to the production of the formic acid.

              14. An apparatus for producing a formate or formic acid from carbon dioxide, characterized in that the apparatus comprises

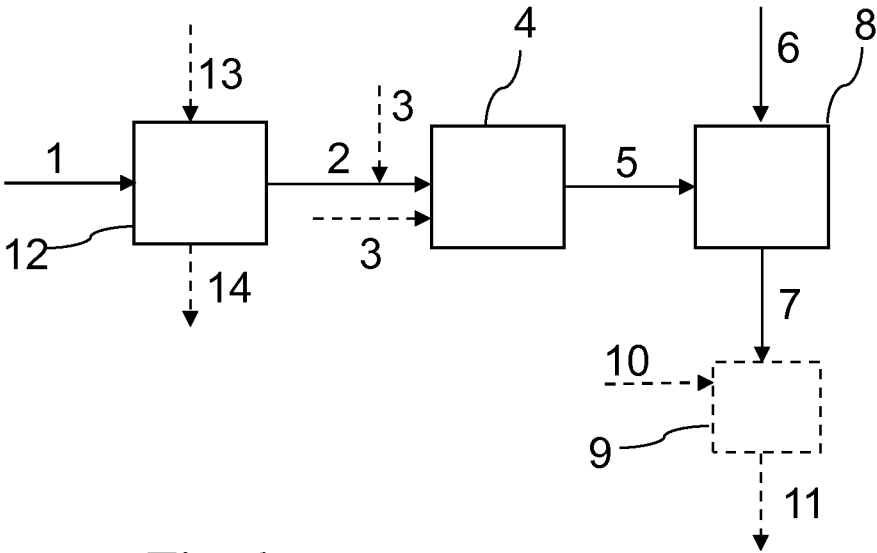
              - at least one equipment (4) into which a mixture 35 (2) which comprises at least carbon dioxide and which further comprises carbonate, ammonia and/or hydroxide (3) is subjected for forming a bicar-

bonate solution (5) comprising at least bicarbonate, and

- at least one reactor (8) in which the bicarbonate solution (5) is treated by a reaction with a metal catalyst at temperature of 10 - 70 °C and pressure of 1 - 100 bar and at least one feeding device for supplying the hydrogen and/or carbon monoxide (6) into the reactor in order to produce the formate (7), and optionally to produce the formic acid (11) from the formate.

15. The apparatus according to claim 14, characterized in that the apparatus comprises at least one capture device (12) or ejector for capturing the carbon dioxide.

- 16. A use of the method according to any one of claims 1 to 13, characterized in that the method is used in a production of formate, in a production of formic acid, in a treatment of captured carbon dioxide, in a production of a chemical or liquid for using as a carrier of carbon dioxide and/or hydrogen, in a production of methanol, or their combinations.



*Fig. 1*

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/FI2021/050810

| <b>A. CLASSIFICATION OF SUBJECT MATTER</b><br><b>INV.</b> C07C51/41 C07C53/06 C07C51/02 C07C53/02<br><b>ADD.</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                                                                                                                                                                         |                                                                             |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------|
| According to International Patent Classification (IPC) or to both national classification and IPC                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                                                                                                                                                                                         |                                                                             |
| <b>B. FIELDS SEARCHED</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                                                                                                                                                                         |                                                                             |
| Minimum documentation searched (classification system followed by classification symbols)<br><b>C07C</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                                                                                                                                                                                         |                                                                             |
| Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |                                                                                                                                                                                         |                                                                             |
| Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)<br><b>EPO-Internal, WPI Data</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |                                                                                                                                                                                         |                                                                             |
| <b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |                                                                                                                                                                                         |                                                                             |
| Category*                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                      | Relevant to claim No.                                                       |
| <b>X</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | <b>US 2016/137573 A1 (LIN HONGFEI [US])</b><br><b>19 May 2016 (2016-05-19)</b><br><b>claims; figures; examples</b><br>-----                                                             | <b>1-16</b>                                                                 |
| <b>X</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | <b>DE 10 2006 030449 A1 (MP NEWCO GMBH [DE];</b><br><b>CALIEBE REINHARD [DE])</b><br><b>4 January 2007 (2007-01-04)</b><br><b>figures</b><br><b>paragraphs [0033] - [0042]</b><br>----- | <b>1-16</b>                                                                 |
| <input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                                                                                                                                                                         |                                                                             |
| * Special categories of cited documents :<br>"A" document defining the general state of the art which is not considered to be of particular relevance<br>"E" earlier application or patent but published on or after the international filing date<br>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)<br>"O" document referring to an oral disclosure, use, exhibition or other means<br>"P" document published prior to the international filing date but later than the priority date claimed<br>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention<br>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone<br>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art<br>"&" document member of the same patent family |                                                                                                                                                                                         |                                                                             |
| Date of the actual completion of the international search<br><br><b>10 February 2022</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                                                                                                                                                                                         | Date of mailing of the international search report<br><br><b>18/02/2022</b> |
| Name and mailing address of the ISA/<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                                                                                                                                                                                         | Authorized officer<br><br><b>Kardinal, Siegmarr</b>                         |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

**PCT/FI2021/050810**

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
|-------------------------------------------|---------------------|----------------------------|---------------------|
| <b>US 2016137573 A1</b>                   | <b>19-05-2016</b>   | <b>NONE</b>                |                     |
| -----                                     |                     |                            |                     |
| <b>DE 102006030449 A1</b>                 | <b>04-01-2007</b>   | <b>NONE</b>                |                     |
| -----                                     |                     |                            |                     |