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(54) Title: METHOD OF TREATING WATER COMING FROM A FISCHER-TROPSCH REACTOR

(57) Abstract: The Fischer Tropsch process is often used for the conversion of hydrocarbonaceous feed stocks into liquid and/or solid hydrocarbons. The feed stock (for example natural gas, associated gas and/or coal-bed methane) is converted in a first step into a mixture of hydrogen and carbon monoxide (this mixture is referred to as synthesis gas or syngas). The syngas is then converted in a second step over a suitable catalyst at elevated temperature and pressure into paraffinic compounds ranging from methane to high molecular weight molecules comprising up to 200 carbon atoms, or, under particular circumstances, even more. In the Fischer-Tropsch (FT) process carbon monoxide and hydrogen are converted into hydrocarbons and water. The water exits a Fischer Tropsch reactor as a waste water stream. The present invention relates to the treatment of said waste water stream.



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METHOD OF TREATING WATER COMING FROM A FISCHER-TROPSCH REACTOR

Field of the invention

The present invention relates to a method for treating waste water obtained from a fixed bed Fischer-Tropsch reactor.

5 Background to the invention

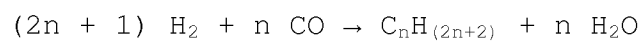
Various processes are known for the conversion of gaseous hydrocarbonaceous feedstocks, especially methane from natural sources, for example natural gas, associated gas and/or coalbed methane, into liquid products, especially methanol and liquid hydrocarbons, particularly paraffinic hydrocarbons. At ambient temperature and pressure these hydrocarbons may be gaseous, liquid and (often) solid. Such processes are often required to be carried out in remote and/or offshore locations, where no direct use of the gas is possible. Transportation of gas, for example through a pipeline or in the form of liquefied natural gas, requires extremely high capital expenditure or is not practical. This holds true even more in the case of relatively small gas production rates and/or fields.

Reinjection of gas will add to the costs of oil production, and may, in the case of associated gas, result in undesired effects on crude oil production. Burning of associated gas has become an undesirable option in view of depletion of hydrocarbon sources and air pollution. A process often used for the conversion of carbonaceous feedstocks into liquid and/or solid hydrocarbons is the well-known Fischer-Tropsch process.

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The Fischer Tropsch process is often used for the conversion of hydrocarbonaceous feed stocks into liquid and/or solid hydrocarbons. The feed stock (for example natural gas, associated gas and/or coal-bed methane) is converted in a first step into a mixture of hydrogen and carbon monoxide (this mixture is referred to as synthesis gas or syngas) . The syngas is then converted in a second step over a suitable catalyst at elevated temperature and pressure into paraffinic compounds ranging from methane to high molecular weight molecules comprising up to 200 carbon atoms, or, under particular circumstances, even more.

In the Fischer-Tropsch (FT) process carbon monoxide and hydrogen are converted into hydrocarbons and water according to the following general reaction:



During the conversion of syngas into paraffinic compounds also water is formed. This water exits the FT reactor as a waste water stream. In case syngas is obtained from natural gas this process is referred to as Gas to liquids (GTL).

Next to the formation of paraffinic hydrocarbons, hydrocarbons containing oxygen can be formed during the Fischer-Tropsch process. These compounds are referred to as oxygenated hydrocarbons or oxygenates. Oxygenates include alcohols, aldehydes, ketones and organic acids. The oxygenates leave the FT reactor in the water stream.

In GTL plants a substantial amount of water is produced by the Fischer-Tropsch process, which exits the FT reactor as a waste water stream. This waste water comprises of oxygenates(organic acids,

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alcohols, aldehydes, ketones) and some free residual hydrocarbons. Due to the presence of oxygenates and hydrocarbons the water requires treatment before it can be discharged. The required water treatment to remove
5 oxygenates from the waste water stream requires elaborate and costly water treatment plants.

Many waste water streams such as those generated by chemical plants, municipal waste and waste water plants, food manufacturing facilities, industrial factories,
10 petroleum refineries and animal farms typically contain high concentrations of organic compounds that need to be removed from such waste streams in view of increasing environmental constraints. Such organic compounds include hydrocarbons and oxygenated hydrocarbons like organic
15 acids, alcohols and aldehydes. In environmental chemistry, the chemical oxygen demand (COD) test is commonly used to indirectly measure the amount of such organic compounds in water, whereby COD is expressed in milligrams per litre (mg/l).

20 Organic compounds that contribute to COD of Fischer-Tropsch waste water can be removed from waste water streams by means of physical, chemical and/or biological processes.

Prior art water treatment systems for Fischer-Tropsch waste water often comprise of distillation followed by an
25 aerobic bio treatment unit. A drawback of an aerobic bioreactor is the required 15-24 hydraulic residence time. Due to the relatively large waste water flow rates in Fischer-Tropsch plant this results in large bio
30 reactors. Further aerobic bio treatment results in large amounts of bio sludge which requires further processing incurring further costs. Aerobic treatment requires continuous air supply to the reactor which is facilitated

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by air blowers. These air blowers require energy resulting in a further increase of the costs for operating an aerobic reactor.

5 An alternative to aerobic bio treatment is anaerobic bio treatment. However treated water from anaerobic bio treatment typically requires post treatment by aerobic bio treatment to meet specification for discharge or reuse.

10 Hence traditionally anaerobic bio treatment is considered economic only for concentrated wastewater streams with COD >5000 mg/l.

15 Efforts are being made to optimize anaerobic bio treatment to obtain treated water quality meeting discharge or reuse specification without aerobic bio treatment. See for example US 8,999,164. However, treated water from anaerobic only system has shown severe fouling characteristics towards subsequent separation steps such as membrane filtration. For example, the fouling characteristics of anaerobically treated effluent leads
20 to very low membrane flux and hence requires a large membrane filtration area which is economically disadvantageous.

Hence there remains a need to improve the treatment of waste water obtained from Fischer-Tropsch process.

25 Summary of the invention

It is an object of the present invention to provide for improvements to the treatment of a waste water stream obtained from at least a Fischer-Tropsch reactor.

30 Accordingly the present invention relates to a method of treating waste water from at least one fixed bed Fischer-Tropsch reactor, said waste water having a COD of 15000-25000 mg/l. Said method comprises the steps of:

a) pre-treating the waste water by:

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i. subjecting said waste water to distillation and/or steam stripping; and

ii. removal of residual wax, preferably by gravity based separation or gas floatation based separation;

5 b) obtaining a pre-treated waste water stream having a COD of maximally 4000 mg/l;

c) feeding said pretreated waste water to a granular sludge based anaerobic bioreactor and subjecting said pretreated waste water to anaerobic bio treatment for
10 maximally 5 hours in which dissolved organic compounds are converted into methane , carbon dioxide and anaerobic biomass;

d) obtaining from the bioreactor:

- bio treated water stream;

15 - a gas stream comprising methane and carbon dioxide wherein, the bio treated water stream has a COD ranging from 20-40 mg/l and suspended solids ranging from 20-50 mg/l and total dissolved solids ranging from 350-600 mg/l;

20 e) removing suspended particles from the bio treated water stream to obtain a treated water stream having a COD <20 mg/l, suspended solids <5 mg/l and Silt Density Index < 5.

The present inventors have found that the method
25 according to the invention provides for good results with respect to water treatment of waste water used in or generated by a chemical reaction.

Detailed description of the invention

The present invention provides for a method of
30 treating waste water obtained from at least one fixed bed Fischer-Tropsch reactor. A substantial amount of water is generated in the Fischer-Tropsch reaction at a commercial scale. These sites are often at remote places. Hence it

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is important that said water can be treated such that it can be utilized at the site. Typically, waste water obtained from a Fischer-Tropsch reactor has a COD of 15000-25000 mg/l.

5 The Fischer-Tropsch reaction produces multiphase product with liquid and gaseous hydrocarbon phases and an aqueous or water phase. The product is subjected to preliminary separation to obtain a segregated aqueous phase. The obtained aqueous or water phase is referred to
10 as the waste water stream. Said waste water stream preferably has a COD of 15000-25000 mg/l.

 The method of the invention comprises as a first step the pretreatment of the waste water. Pretreatment includes as a first step subjecting said waste water to
15 distillation and/or steam stripping. By distillation or steam stripping volatile compounds such as alcohols, aldehydes and ketones are removed from the waste water. In this step part or substantially all alcohols, aldehydes and ketones are removed from wastewater and
20 exit the unit from the top. The removed organics may be burnt as fuel. The effluent stream from the bottom of the distillation or stripping step contains organic acids and light alcohols and traces of other heavier oxygenates. The COD of this stream (the effluent) is maximally
25 4000mg/l but may be lower and may vary from 1000-2000 mg/l.

 After steam stripping and/or distillation the water is cooled and residual wax present in the water is removed. Removal of the residual wax can be achieved by
30 gravity based separation or gas (for example: nitrogen) floatation based separation. Separators such as API separator or a dissolved gas floatation unit may be used. The residual wax is obtained and can be reheated and

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processed in hydrocarbon processing facilities which may be part of the chemical plant. In this step gravity based separation or gas floatation based separation is used to ensure that substantially all wax and other free hydrocarbons are removed prior to bio treatment. The water obtained after these steps is referred to as pre-treated waste water stream. This pre treated waste water stream has a COD of maximally 4000 mg/l.

In an aspect of the invention the COD of the pretreated water stream ranges from 500-3000mg/l and preferably ranges from 1000-2000mg/l.

After the residual wax and other free hydrocarbons have been removed the pre-treated waste water stream is subjected to anaerobic bio treatment in a bio reactor. During anaerobic treatment the organic compounds present in the water are converted by microorganisms into methane, carbon dioxide and biomass. During the bio treatment anaerobic microorganisms convert dissolved organics into biogas comprising methane and carbon dioxide and water vapor. The bio treated water and the bio gas comprising methane/carbon dioxide comprising gas mixture are withdrawn from the reactor. Said biogas can for example be used as fuel gas or converted into syngas and used in the Fischer-Tropsch process.

The anaerobic biotreatment process generates compared to aerobic treatment according to the prior art, low amounts of waste sludge. Moreover anaerobic processes require up to 1/10th reactor volumes compared to aerobic processes.

Traditionally, anaerobic biotreatment is considered economically viable for concentrated feed streams with COD of excess of 5000 mg/l. It is known that the anaerobic bio treatment kinetics is slower than aerobic

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bio treatment and hence relies on higher substrate concentration for faster (commercially viable) rates. Moreover the treated water quality observed in an anaerobic reactor is not sufficient for disposal or reuse. It generally requires another aerobic bio treatment step which is economically disadvantageous. Hence for lower COD concentration only aerobic biotreatment is generally considered.

The bio treated water stream has a COD ranging from 20-40 mg/l and suspended solids ranging from 20-50 mg/l and total dissolved solids ranging from 350-600 mg/l. The inventors found that an anaerobic bio treatment step can be utilized to obtain water that can be reused or disposed of. It is preferred that the water is treated only once anaerobically. Preferably the water is not subjected to any further biological treatment. Hence in an aspect of the invention the method according to the present invention comprises only one biological treatment step being current step c).

The bio treated water is further treated by removing (step e) suspended particles from the bio treated water stream. The water obtained after removal of the particles is referred to as treated water stream and has a COD of less than 20 mg/l , suspended solids of less than 5 mg/l and a Silt Density Index (SDI) of less than 5. The SDI is measured in accordance with ASTM Standard D4189 and is a measure for the fouling capacity of water in reverse osmosis systems. Hence, the treated water is suitable to be fed to a reverse osmosis unit.

The present inventors have found that the water obtained with the method according to the present invention is of very good quality. The quality is such that the water can be reused in the cooling of the

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different stages of the gas to liquids process but can also be used as irrigation water for irrigating the plant site.

5 In an aspect of the present invention salts present in the treated water stream obtained in step e), are removed from the treated water stream. This is preferably achieved by subjecting the treated water to reverse osmosis and/or ion exchange.

10 The waste water stream comprises oxygenated compounds, such as alcohols, aldehydes, ketones and organic acids and more specifically comprises methanol, ethanol, propanol, formaldehyde, acetaldehyde, propaldehyde, formic acid, acetic acid and propionic acid. Typically, these compounds are present in waste
15 water obtained from chemical reactors such as Fischer-Tropsch reactors.

In an aspect of the invention the waste water is subjected to at least distillation in at least one distillation column. During distillation a concentrated
20 vapor stream is obtained at the top of the distillation column and a stream primarily containing acidic oxygenates is obtained at the bottom of the distillation column. The stream containing acidic oxygenates is used for further treatment.

25 In an aspect of the invention the waste water obtained from the at least one fixed bed Fischer-Tropsch process has a pH ranging from 3-4 and the treated water stream obtained in step e) has a pH ranging from 6.5 to 8.5.

30 In an aspect of the invention the pretreated waste water is subjected to an anaerobic bio treatment for a period ranging from 2 to 4 hours. The inventors have

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found that advantageously good results are obtained such short periods of bio treatment.

In an aspect of the invention the suspended particles in step e) are removed by at least filtration
5 (microfiltration or ultrafiltration) of the bio treated water stream with an average normalized flux of at least $50 \text{ LH}^{-1}\text{m}^{-2}\text{bar}^{-1}$.

Preferably, a membrane used in microfiltration or ultrafiltration comprises at least a material selected
10 from the group consisting of poly vinyl-idene chloride (PVDF), poly-acronitrile (PAN), poly-ether sulfone (PES), poly-tetra fluoroethylene (PTFE) or ceramics including silicon carbide (SiC) or alumina. Preferably, the filter comprises a filtration element which is
15 selected from the group consisting of flat sheet, tubular or hollow fiber. The filtration step may be operated in cross flow or dead end filtration mode.

In an aspect of the invention the treated water of step e) is subjected to at least reverse osmosis
20 obtaining at least 80% of the water of the treated water as a first stream and a concentrate stream. It is preferred that the reverse osmosis is performed such that said obtained first water stream has a conductivity of 10 microS/cm or less.

The obtained concentrate stream may be subjected to
25 evaporation and crystallization in order to recover at least 90 vol% of the water present in the concentrate stream, preferably having a conductivity of maximally 40 microS/cm. This further improves the efficiency of
30 recovery of fresh water.

Evaporation may be carried out in evaporators such as forced circulation, falling film, natural circulation,

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rising film, plate, horizontal wetted, combination types, multi-stage flash or multi-effect distillation.

In this step the salt content of the concentrate stream from step e) is further increased by evaporation of water. The evaporated water is condensed and recovered. While evaporating the water, the salt content of the concentrate stream is increased and may be increased to close to the saturation point of the salts.

Subsequently the concentrate stream from evaporator is sent to a crystallizer where further evaporation of water leads to crystallization of salts and a solid salt product stream is obtained.

The crystallizer may be adiabatic vacuum, evaporative forced, draft tube baffle type, spray evaporator crystallizer or Oslo type.

The obtained salt can be disposed or reused depending on the composition of the salt. The obtained salt may be re-used as ice-melting salts or as feedstock for the manufacturing of industrial chemicals.

With a fixed bed Fischer-Tropsch reactor is meant a reactor comprising one or more reaction tubes filled with a catalyst. The catalyst is catalytically active in a Fischer-Tropsch reaction. The catalyst present in the fixed bed in the reactor from which the waste water is obtained, preferably comprises a cobalt based catalyst and may further comprise promoters such as zirconium, titanium, chromium, vanadium and manganese. The catalyst particles may further comprise a carrier material. The catalyst carrier is preferably porous, such as a porous inorganic refractory oxide, more preferably alumina, silica, titania, zirconia or combinations thereof.

While the invention has been described in terms of what are presently considered to be the most practical

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and preferred embodiments, it is to be understood that the disclosure need not be limited to the disclosed embodiments. It is intended to cover various modifications, combinations and similar arrangements included within the spirit and scope of the claims, the scope of which should be accorded the broadest interpretation so as to encompass all such modifications and similar structures. The present disclosure includes any and all embodiments of the following claims.

It should also be understood that a variety of changes may be made without departing from the essence of the invention. Such changes are also implicitly included in the description. They still fall within the scope of this invention. It should be understood that this disclosure is intended to yield a patent covering numerous aspects of the invention both independently and as an overall system and in both method and apparatus modes.

In addition, as to each term used, it should be understood that unless its utilization in this application is inconsistent with such interpretation, common dictionary definitions should be understood as incorporated for each term and all definitions, alternative terms, and synonyms such as contained in at least one of a standard technical dictionary recognized by artisans.

The appended claims form an integral part of the description by this reference.

The invention is illustrated by the following non-limiting examples.

Examples

Experiment 1 (invention)

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Tests with anaerobic biotreatment on GTL wastewater were conducted. The testing was done on a 60 liter reactor. Reactor feed COD was between 1200-1500 mg/l comprising of organic acid (86%) and alcohol (14%) representing Fischer-Tropsch reaction water after distillation. The reactor was operated at 33°C. The reactor feed pH was controlled at 6 by dosing 4% NaOH solution. Trace Ammonia, phosphorous and trace nutrients were continuously added.

The results show excellent treated water quality within a short hydraulic residence time of an anaerobic reactor.

The experiments showed that good water quality can be obtained with an anaerobic treatment with hydraulic residence time of 2.5 hrs. The treated water has an average COD of 35 mg/l, average suspended solids of 25 mg/l and pH of 7.5 and can be directly reclaimed without the need of polishing by aerobic reactor. The obtained water is fit for reuse at a commercial GTL sites.

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C L A I M S

1. A method of treating waste water from at least one fixed bed Fischer-Tropsch reactor, said waste water having a COD of 15000-25000 mg/l, the method comprising the steps of:

- 5 a) pre-treating the waste water by:
- i. subjecting said waste water to distillation and/or steam stripping; and
- ii. removal of residual wax, preferably by gravity based separation or gas floatation based separation;
- 10 b) obtaining a pre-treated waste water stream having a COD of maximally 4000 mg/l;
- c) feeding said pretreated waste water to a granular sludge based anaerobic bioreactor and subjecting said pretreated waste water to anaerobic bio treatment for
- 15 maximally 5 hours in which dissolved organic compounds are converted into methane , carbon dioxide and anaerobic biomass;
- d) obtaining from the bioreactor:
- bio treated water stream;
- 20 - a gas stream comprising methane and carbon dioxide;
- wherein, the bio treated water stream has a COD ranging from 20-40 mg/l and suspended solids ranging from 20-50 mg/l and total dissolved solids ranging from 350-600 mg/l;
- 25 e) removing suspended particles from the bio treated water stream to obtain a treated water stream having a COD <20 mg/l , suspended solids <5 mg/l and Silt Density Index < 5.

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2. The method according to claim 1 wherein the anaerobic reactor can be chosen from upflow anaerobic sludge blanket reactor, expanded granular sludge bed reactor or internal circulation reactor.

5 3. The method according to claim 1 wherein the waste water has a COD of 15000-25000 mg/l.

4. The method according to any one of the preceding claims wherein the waste water comprises oxygenated compounds, preferably said oxygenated compounds comprise
10 alcohols, aldehydes, ketones and organic acids and more preferably comprises at least methanol, ethanol, propanol, formaldehyde, acetaldehyde, propaldehyde, formic acid, acetic acid and propionic acid.

5. The method according to any one of the preceding
15 claims, wherein the waste water is subjected to at least distillation in at least one distillation column and wherein a concentrated vapor stream is obtained at the top of the distillation column and a stream primarily containing acidic oxygenates is obtained at the bottom of
20 the distillation column.

6. The method according to any one of the preceding claims wherein the COD of the pretreated water stream ranges from 500-3000mg/l and preferably ranges from 1000-2000mg/l.

7. The method according to any one of the preceding
25 claims wherein the waste water has a pH ranging from 3-4 and the treated water stream obtained in step e) has a pH ranging from 6.5 to 8.5.

8. The method according to any one of the preceding
30 claims wherein the pretreated waste water is subjected to

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an anaerobic bio treatment for a period ranging from 2 to 4 hours.

9. The method according to any one of the preceding claims wherein the suspended particles in step e) are removed by at least filtration (microfiltration or ultrafiltration) of the bio treated water stream with an average normalized flux of at least $50 \text{ LH}^{-1}\text{m}^{-2}\text{bar}^{-1}$.

10. The method according to claim 9 wherein a membrane of the microfiltration or ultrafiltration step comprises at least a material selected from the group consisting of poly vinyl-idene chloride (PVDF), poly-acronitrile (PAN), Poly-ether sulfone (PES), poly-tetra fluoroethylene (PTFE) or ceramics including Silicon Carbide (SiC) or Alumina.

11. The method according to claim 9 or 10 wherein the filter comprises a filtration element which is selected from the group consisting of flat sheet, tubular or hollow fiber.

12. The method according to any one of claims 9-11 wherein the filtration can be operated in cross flow or dead end filtration mode.

13. The method according to any one of the preceding claims wherein salts are removed from the treated water stream of step e) by subjecting the treated water to reverse osmosis and/or ion exchange.

14. The method according to any one of the preceding claims wherein the treated water of step e) is subjected to at least reverse osmosis obtaining at least 80% of the water of the treated water as a first stream and a concentrate stream, preferably said obtained water has a conductivity of 10 microS/cm or less.

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15. The method according to claim 14 wherein the
concentrate stream is subjected to evaporation and
crystallization in order to recover at least 90 vol% of
the water present in the concentrate stream preferably
5 having a conductivity of maximally 40 microS/cm.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

INV. C02F3/28 C02F9/00
ADD. C02F1/04 C02F1/44 C02F101/32 C02F103/36 C02F101/34
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C02F

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)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	WO 03/106354 A1 (SASOL TECH PTY LTD [ZA]; DANCUART KOHLER LUIS PABLO FID [ZA]; DU PLESS) 24 December 2003 (2003-12-24) page 17, line 18 - line 23 -----	1-15
A	CN 101 190 821 B (CHINA PETROCHEMICAL CO LTD [CN]) 25 January 2012 (2012-01-25) paragraph [0030] - paragraph [0045] ----- -/-	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

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Name and mailing address of the ISA/

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One1 Inda, Santiago

INTERNATIONAL SEARCH REPORT

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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