Title: PROCESS FOR SIMULTANEOUS RECOVERY AND CRACKING OF OIL FROM OIL/SOLID MIXTURES

Abstract: The present invention relates to a process for simultaneous recovery and upgrading/cracking of oil from solids, such as tar sand, oil shale and other oil/solids mixtures.
PROCESS FOR SIMULTANEOUS RECOVERY AND CRACKING OF OIL FROM OIL/SOLID MIXTURES

The present invention is related to a process for "dry" recovery of oil from tar sand (also called oil sands), oil shale and other oil solids mixtures and with simultaneously upgrading of the oil in the same process.

Tar sand is found in enormous quantities in a number of countries, but the greatest resources are found in Canada and consists of heavy oil and sand in natural resources in different depths. These resources have been subject for intensive research in developing technologies for recovery of the oil from the sand. Thus, a number of different technologies exist.

Alberta's most important mineral resources are oil and natural gas, and they account for about 90 percent of Alberta's income from mining. Alberta produces approximately two-thirds of Canada's oil and more than three-quarters of its natural gas. Nearly half of Alberta's oil is mined from vast oil sands, which are deposits of a heavy crude oil called bitumen. Alberta's oil sands represent the largest known deposits of bitumen in the world. The oil sands occur in three major areas of the province: the Athabasca River Valley in the northeast, the Peace River area in the north, and the Cold Lake region in east central Alberta. Bitumen is more costly to mine than conventional crude oil, which flows naturally or is pumped from the ground. This is because the thick black oil must be separated from the surrounding sand and water to produce a crude oil that can be further refined.

During the 1950s and 1960s, oil deposits were discovered in other regions, such as the Peace River area and the Swan Hills, south of Lesser Slave Lake. By the late 1960s the last major oil deposits had been found.

The bitumen, which contrary to normal crude found in deep reservoir, does not have the same light fractions as these have been evaporated off over thousands of years. The bitumen thus consists of heavy molecules with a density of over 1.000 kg/dm³ (less than 10 API) and a viscosity 1000 times higher than light crude. In addition the tar sand contains sulphur over 4 w% and hundreds of ppm with heavy metals. The content of organic matter in tar-sand can range from 5 w% up to 20 w% and thus extraction of oil from tar sand involves huge mass transport.
2

Because of the composition of the bitumen, it has to be upgraded into synthetic crude before it can be refined in a refinery for the production of different oil products.

Because of the economical potential of these huge resources, a number of different processes exist for the recovery of oil from tar sand. Such technologies involve biological, solvent, thermal and processes where the oil is washed out of the sand by superheated water and which requires about 430 litres of water for every barrel of oil produced.

Because of the enormous tailings (sand and spent contaminated water) associated with tar sand extraction, the different processes faces a number of environmental constrains. In addition, present technologies generate huge amount of so called green house gases.

Contrary to tar sand, oil shale is shale containing organic matter known as kerogens which can not be washed or dissolved as for the bitumen in tar sand. To recover oil from oil shale, it must be heated to a temperature of 500 - 600 C whereby the organic matter is cracked into liquid products. As for tar sand, oil shale contains a number of unwanted constituents, which causes environmental constrain. And as for technologies in recovering oil from tar sand, there exist a number of different technologies in recovering oil from oil shale.

The present invention is related to an energy self sustained process where a number of the obstacles with the existing technologies are solved and which in addition to the oil recovery, upgrades the oil into a lighter product than any other existing technologies, removes sulphur in the order of 40% and heavy metals in the order of 90% and without the use of water as is the case with the dominating processes. The process disposes off dry tailings with limited environmental constraints as the inorganic matter (sand) is disposed off in dry condition.

The process comprises the following components:

1. HOPPER ARRANGEMENT
2. FLUIDIZING REACTOR WITH
   a. Start up combustor with
      i. Air supply system
      ii. Gas supply system
3. CYCLONE
4. SAND FILTER TYPE "OTTO"
5. SOLID GAS HEATER WITH
The above mentioned components are illustrated in Figure 2.

**PROCESS DESCRIPTION**

The present invention relates to a process for the simultaneous extraction and upgrading of oil from oil sand, oil shale and other particle-oil mixes (e.g. sludge) in one operation, without the use of water or steam.

When the process has reached its steady-state level, shredded oil sand or oil shale is injected into a vertical REACTOR where it meets a bubbling bed of hot sand.
A part of the discharged sand can be mixed with the oil sand in order to homogenize and pre-heat the feed.

When the oil sand meets the hot bubbling bed, the oil is stripped off at a temperature of about 360°C for oil sand and about 450°C for oil shale because of the partial pressure conditions in the reactor caused by the composition of the gas injected into the REACTOR'S plenum.

When the oil is stripped off in the reactor, it undergoes a partial cracking because of the thermal and kinetic effects in the reactor and rapid movement by flash evaporation of original water in the sand. As the process operates at 1.1 bar, superheated steam is produced which, due to the low pressure, expands violently, causing thousands of explosions which generate extreme mechanical shear forces between the sand grains on the surface of the bubbling bed, whereby cracking takes place.

The sand is conveyed pneumatically into a RISER by the hot gases injected into the REACTOR and the oil-gas generated in the reactor. The gasses injected into the REACTOR can be the gasses formed by extraction of the oil and water in the oil sand or any kind of a neutral gas such as nitrogen, argon or helium or steam. These gasses are circulated in the system as described below.

If needed, a portion of the produced oil in the oil condenser can be pumped to a hydraulic atomization nozzle located on the RISER for a second upgrading of the oil.

Because of the low partial pressure of the oil-gas in the reactor, the process can operate at a temperature of about 360°C for oil sand and about 450°C for oil shale in the reactor. Hence, the process greatly reduces energy requirements, together with the related costs and pollution.

The stream of oil-gas, steam from original water in the sand and the injected gas into the REACTOR are routed to a CYCLONE where the sand is separated from the stream and discharged to a SOLID GAS HEATER.
The sand which builds up in the REACTOR is continuously discharged into the SOLED GAS HEATER.

From the CYCLONE the gasses are routed to a SAND FILTER which removes sand carried over from the CYCLONE. The trapped sand in the SAND FILTER is discharged to the SOLID GAS HEATER.

The solid-free gases are then transported to a dual condensation system. In the first condenser, the oil-gas is condensed into liquid oil in the OIL CONDENSER and the steam is condensed into water in the STEAM CONDENSER. This dual condensing procedure eliminates the formation of an emulsion, which would have occurred with a single condensation system.

The produced oil is continuously discharged from the OIL CONDENSER by a discharge pump to the RECEIVING TANK.

The produced water is continuously discharged from the WATER CONDENSER by a discharge pump to a DECANTER where light oil fractions carried over are pumped off and routed to the RECEIVING TANK.

Before the gases enters the OIL CONDENSER, a part of the gas which mainly consists of oil gas is sucked off by a SUCTION FAN and injected into an EXHAUST HEAT EXCHANGER at a temperature of ca. 200°C.

In the EXHAUST HEAT EXCHANGER, the gas is heated to about 250°C and is routed to the SOLID GAS HEATER where it is heated to about 350°C by extracting heat from the sand injected into the heater.

From the heater, the gas is routed to a FLUIDIZED SUPER HEATER where the gas is heated to about 600°C and routed to the plenum in the REACTOR where the hot gas is delivering the energy for the extraction of the oil and water from the sand.
The energy for the FLUIDIZED SUPER HEATER is delivered by combustion of oil and/or gas and oil contained in raw oil sand which is injected into the fluidized bed in the heater.

The research and development work has proven the technology in a test where oil sand oil with an initial grade of 10 API was extracted at 360°C and upgraded in the reactor to 18 API oil and then in the riser to 25 API oil. Upgrading oil from 10 API to 25 API approximately doubles the gross value of the oil.

The process generates 20-30% less CO₂ than existing oil sand recovery processes. To optimise collision between the particles as to obtain maximum shear forces between the solids in the stream of sand, the gasses are accelerated and retarded in a riser of varying diameters.

The collision between the particles give rise to a mild hydrogenation of the oil by sonoluminescence of microscopic steam bubbles trapped between the colliding solid particles. When steam bubbles are trapped between unevenness in the tumbling particles, the steam is subject to an adiabatic compression whereby the temperature and pressure in the bubble is raised several thousand times above overall temperature and pressure in the process. This causes water to enter into a supercritical state where water is cracked into hydrogen and hydroxyl radicals. Hydrogen, which is absorbed by the heavy oil chains, reduces their bonding whereby the impact forces from the tumbling grains and the "explosion" of the microscopic steam bubbles can crack the hydrocarbon molecules. The majority of the hydrogen is then released and react back with the hydroxyl radicals into water, but a part of the hydrogen causes a mild hydrogenation of the product.

Hydrogen is also released in the REACTOR and the FLUIDIZED SUPERHEATER and in the SOLID GAS HEATER by:

\[ C + H_2O = H_2 + CO -131,38 \text{ kJ/kg mol carbon} \]

The water-gas shift reaction \[ CO + H_2O = CO_2 + H_2 - 41,98 \text{ kJ/mol} \]
It is highly desirable to achieve good sand/oil mixing as early and as quickly as possible. The method described to achieve this requires the above-mentioned acceleration and retarding of the stream. Traditionally, steam is the medium used to maintain solid bed fluidity and movement in the riser. Steam, however, has a deleterious effect on the very hot solids that is met in residue cracking processes. Under these conditions steam causes hydrothermal deactivation of the catalyst in for example FCC-crackers.

This is overcome by the present invention by the recirculation and heating of a part of the gas stream from the fluidised bed reactor which mainly consists of hydrocarbon gases or a mixture of neutral gases as the carrier of the solids, which act as a catalyst in cracking of the oil.

To have the process verified, a 2.5x2.5x3 m test rig was built and located at SINTEF ENERGY RESEARCH AS in Trondheim, Norway with a maximum power of 50 kW.

The rig used during testing is shown in Figure 4.

The energy requirement to process one kg of oil sand is given by:

\[ Q = x_s * c_s * dt + x_o (c_s * dt + r_o) + x_w * H \]

Where:
- \( x_s \) = weight part sand (including metals and sulphur), example 80%
- \( X_o \) = weight part oil, example 15%
- \( x_w \) = weight part water, example 5%
- \( c_s \) = specific heat of sand kJ/kgK = 1 kJ/kgK
- \( C_0 \) = specific heat of oil at operating temperature kJ/kgK = approx 2.25 kJ/kgK
- \( r_o \) = heat of evaporation kJ/kg = approx 225 kJ/kg
- \( dt \) = temperature difference between operating temperature and feed temperature of sand K
- \( H \) = enthalpy of water at operating temperature kJ/h = 3500 kJ

Operating temperature 360 C = 633 K

The tests were carried out with tar sand from the Athabasca River Valley deposits with the properties listed above where the following results were obtained:
Density of oil recovered from the fluidiser: 18 API.
Density of oil recovered in the riser: 29.3 API.
Density of oil drained from the oil condenser: 25.15 API.
Remaining coke in spent sand 1.25 W%.
5 Reduction of sulphur in the oil: 45%
Reduction of heavy metals: 87%

The oil sand, recovered oil and clean sand resulting from the test are illustrated in Figure 5.

The process according to the invention will be described in more detail with reference to the drawings, wherein:

Figure 1 shows a simplified flow diagram of the process according to the invention.
Figure 2 shows another illustration of the process according to the invention.
Figure 3 shows an example of a more complete flow diagram of a process designed for both oil sand and oil shale operation.
Figure 4 shows the test rig used during the testing of the process.
Figure 5 shows the oil sand, recovered oil and clean sand resulting from the test.

The process is described further in the simplified flow diagram in Fig. 1.

A) shows the vertical fluidised reactor which has a fluidising mesh B) a portion from the bottom of the vessel. The space between the bottom and the fluidised mesh B) is a plenum C) which is receiving the hot gases from the fluidized super heater D) which can be fuelled either by gas and/or recovered oil in addition to the oil in raw oil sand injected into the super heater from a hopper E). The hot gasses will heat and fluidise the solids (sand) F) entrained in the reactor A). The pressure from the hot gases built up in the reactor, will cause the solids and its entrained gases which consists of steam and hydrocarbon gasses, to be pneumatically transported through a riser G) into a reactor cyclone H) which is designed in such a manner that contrary to ordinary cyclones, the solids are spinning several hundred times in the cylindrical part of the cyclone before they falls down the conical part I) and into a solid gas heater J).

In the reactor A is arranged a plate 1) across the reactor a distance from the fluidizing mesh B) and the top of the reactor A). The plate will act as a "waterlock" whereby a
particle which is injected on the shown right side of the plate, has to move down and under the plate before it enters the entrance of the riser S). This arrangement ensures that sufficient retention time is obtained to ensure that all hydrocarbons associated with the sand and/or shale, are evaporated off.

Oil sand is injected into the reactor A) from a hopper K). The same amount of sand injected into the reactor A) and which is not carried over to the cyclone H) has to be drained from the reactor. This is done through the pipe arrangement KK) where the sand is transported to the solid gas heater J). The cooled sand from J) is discharged at the bottom through the pipe KKK).

From the reactor cyclone H) and the sand filter L) the gaseous stream is routed to an oil condenser M) which is set to a temperature were the majority of the oil gas is condensed into liquid oil. The gas is condensed by the mean of the recovered oil as the oil collected at the bottom of the condenser is pumped by the pump N) through a heat exchanger O) and cooled by water delivered by the pump P). From the heat exchanger O), the cooled oil is routed to the top of the condenser and condenses the incoming oil gasses. As the level of the oil rises in the condenser, the product is drained off through the pipe Q) by the pump QP).

The steam is routed to a second condenser R) which is cooled by water injected from the pump P). The steam is condensed by means of the condensed steam as the water collected at the bottom of the condenser is pumped by the pump PP) through a heat exchanger WH) and cooled by water delivered by the pump P). From the heat exchanger WH), the cooled water is routed to the top of the condenser and condenses the incoming steam with associated light oil fractions. Condensed water is drained off from the condenser through the pipe S) by the pump SP) and is collected in a settling tank T). In the settling tank T), light oil brought over from the steam condenser R) will be decanted off through the pipe U) to a receiver tank V). Water is drained off through the pipe W) to drain.

Non-condensable matter in the condenser R) is exhausted through the pipe X) either to air or to a gas cleaning system Y) depending on the local emission requirements.
A portion of the product is returned to the riser G) through the pipe NN) by a high pressure pump LL) to the atomisation nozzle S) attached to the riser G).

Before the gas stream after the filter L) enters the oil condenser M), a portion of the gas is sucked off by the suction fan AA) and is routed to an exhaust heater BB) where the gas is heated by heat exchange of the exhaust gas from the fluidized super heater D).

From the exhaust heat exchanger BB), the gas is routed to the solid gas heater J) where the gas is further heated by heat exchanged from the sand collected in J).

From the solid gas heater J), the gas is routed to fluidized super heater D) where the gas is heated to the target temperature by heat exchange from combusted oil and/or gas injected into the heater D) by the pump CC) and the combustion of oil in raw oil sand delivered to the heater D) by the hopper E). Spent sand from the super heater D) is routed to the solid gas heater J) via the pipe JJ).

From the fluidized super heater D) the hot gas(es) is/are routed to the plenum C) in the reactor A) where it delivers the energy for the process by heat exchange with the injected oil sand from the hopper K).

By varying the composition of the hot gas, the partial pressure in the reactor can be adjusted to the optimal conditions for different feeds.

To obtain the abovementioned acceleration and retarding of the stream in the riser, this can be obtained by giving the riser varying diameters. One preferred embodiment is to form a part of the riser as a Laval nozzle where the atomisation nozzle(s) S) is (are) located either in the narrowest part of the ejector or where the ejector starts to expand.

The entire process is a high intensive thermal process with a high energy density because of the velocity of the gas and sand stream. Because of the velocities in the process, the intensive heat exchange between sand and oil and the low partial pressure of the hydrocarbon gasses caused by the composition of the injected hot gases and
produced hydrocarbon gases, the process can operate at a temperature in the range of 300 - 500°C. Apart from reduced thermal stress and energy consumption, this low temperature reduces polymerisation of the cracked product.

Start up of the process is done by the combustors DD) and EE) to heat the entire system to designed process temperature. When the temperatures in the different components are reached, the process is turned into process mode and the combustors are shut off.

Fig. 3 shows an example of a more complete diagram for a plant designed for both oil sand and oil shale operations with heat recovery and gas cleaning.

2) shows the pit where the material is mined. The material is hauled to a crusher 3) where larger stones are removed and minor stones are crushed to required size. From the crusher 3) the material is conveyed to a silo arrangement 4) from where it is conveyed to the hopper 4). Form the hopper, the material is injected into the reactor 5) by a conveying device 6) which can be a screw conveyor or other means.

The material is distributed onto the fluidizing bed 7) on the shown left side of the "waterlock" plate 8) whereby the inorganic grains has to move from the surface of the bed, under the plate and up to the entrance of the riser 9).

The fluidization gasses in the reactor 5) transport the injected material into the riser 9) and into the reactor cyclone 10) and further on to the sand filter 11) and further on to the oil condenser 12).

Under the reactor 5) (or on its side) is arranged the fluidized superheater 13). To the superheater is attached a combustor 14) for start up. The combustor can either be a gas or oil combustor.

When the process has reached its steady state, a portion of the gas after the filter 11) is sucked over to the superheater 13) by a suction fan 15) into the plenum 17) on the superheater/regenerator 13).
As coke is formed on the sand in the superheater 13) coming from the cyclone 10), the gas or oil to the combustor 14) is reduced whereby the injected air starts to combust the formed coke in the superheater 13). Control of the heat released by the coke combustion, is done by the gas pulled over by the suction fan 15) which can pull over gas before it reaches the oil condenser and after the steam condenser 16).

The gases formed in the superheater 13) is transported to the fluidizing mesh 17) on the reactor 5).

The spent inorganic particles are charged out the superheater 13) into the gas heat exchanger 18). The latent heat in the sand in the gas heat exchanger 18) is utilized for steam production for external use, either for production of electricity or other purposes. In the shown diagram the steam exiting the gas heat exchanger 18) is routed to a steam turbine 19) driving a generator set. The exhaust steam from the turbine 19) is routed to a condenser 20) which condenses the steam to water which is pumped back to the gas heat exchanger 18) by the pump 21). Makeup water to the boiler in the gas heat exchanger 18) is delivered from the water treatment unit 22) which receives water from cooling water exiting the oil/water heat exchanger 33). Cooling water is also used as condensation medium for the condenser 20.

In the oil condenser 12) the temperature is set at about 95°C whereby the oil is condensed and discharged from the condenser 12) by the pump 22) to a holding tank (not shown). A portion of the produced oil is pumped off by the pump 23) to an atomization nozzle 24) on the riser 9).

The steam and non-condensable gases are routed to the steam condenser 16) where produced water is condensed. The produced water is pumped off by the pump 24) to a decanter 25) where decanted oil is pumped to the oil holding tank by the pump 26). The oil free produced water is now transported to a concrete mixer 27) where it is mixed with spent sand from the cyclone 28). The sand is pneumatically brought to the cyclone 28) by the air compressor 29) at the gas heat exchanger 18).
From the steam condenser 16), the non condensable gasses are routed to an electrostatic precipitator 30) where possible oil aerosols are captured and conveyed to the oil condenser 12).

From the electrostatic precipitator 30) the gasses are transported to the gas cleaning unit 31).

The heat of condensation in the steam condenser is removed by the water/water heat exchanger 32) and the oil/water heat exchanger 33).

The cooling water to the heat exchangers is delivered by the pump 34).
Claims:

1. A process for simultaneously recovery and cracking/upgrading of oil from solids such as tar sand, oil shale and other oil/solids mixtures, characterized in that oil containing solids are injected into a fluidised bed reactor where the hydrocarbons are evaporated off and where the heat for the evaporation is delivered by heated off drawn gases from the gas stream and being injected into the reactors plenum and where these gases together with the evaporated hydrocarbons act as a pneumatic carrier of the solids and reduces the partial pressure of the hydrocarbon gases and where the stream is routed to a cyclone reactor and further to a solids removal separator and further to a condensing system for the condensable gasses.

2. The process for simultaneously recovery and cracking/upgrading of oil from solids such as tar sand, oil shale and other oil/solids mixtures in accordance with claim 1, characterized by that the composition of the heated gases is adjusted by a mixture of neutral gases such as nitrogen, argon, helium, steam and other suitable gases in order to give the optimal partial pressure in the reactor for the different feeds.

3. The process for simultaneously recovery and cracking/upgrading of oil from solids such as tar sand, oil shale and other oil/solids mixtures in accordance to claim 1, characterized in that the temperature in the superheater/regenerator is controlled by the injected oil sand into the regenerator and gasses drawn off from the produced gasses before and after the condensers.

4. The process for simultaneously recovery and cracking/upgrading of oil from solids such as tar sand, oil shale and other oil/solids mixtures in accordance to claim 1, characterized in that the oil stripped sand is routed to a heat exchanger for the pre heating of the hot gases to be injected into the plenum of the reactor.

5. The process for simultaneously recovery and cracking/upgrading of oil from solids such as tar sand, oil shale and other oil/solids mixtures in accordance with any of claims 1 and 4, characterized in that the gas is drawn off from the process to be heated by heat exchange in an exhaust heater heated by exhaust from a super...
heater fuelled by combustion of oil or gas and oil contained in raw oil sand injected into the super heater.

6. The process for simultaneously recovery and cracking/upgrading of oil from solids such as tar sand, oil shale and other oil/solids mixtures in accordance with any one of claims 1, 4 and 5, characterized in that the preheated gases from the exhaust heater and the sand heat exchanger is routed to a super heater where it is heated to target temperature by heat exchange from combusted oil or gas and oil contained in raw oil sand injected into the super heater.

7. The process for simultaneously recovery and cracking/upgrading of oil from solids such as tar sand, oil shale and other oil/solids mixtures in accordance with claim 1, characterized in that a plate is arranged in the reactor forcing the particles down and under the plate before they enter the exit entrance whereby optimal retention time is achieved for the evaporation of the hydrocarbons associated with the inorganic particles.
AMENDED CLAIMS
received by the International Bureau on 04 June 2010 (04.06.2010)

1. A process for simultaneously recovery and cracking/upgrading of oil from solids such as tar sand, oil shale and other oil/solids mixtures, wherein oil containing solids is injected into a fluidised bed reactor where the hydrocarbons are evaporated off, characterised in that the heat for the evaporation is delivered by heated off drawn gases from the gas stream and being injected into the reactors plenum and where these gases together with the evaporated hydrocarbons act as a pneumatic carrier of the solids and reduces the partial pressure of the hydrocarbon gases and where the stream is routed to a cyclone reactor and further to a solids removal separator and further to a condensing system for the condensable gasses and wherein the composition of the heated gases is adjusted by a mixture of neutral gases such as nitrogen, argon, helium, steam and other suitable gases in order to give the optimal partial pressure in the reactor for the different feeds.

2. A process for simultaneously recovery and cracking/upgrading of oil from solids such as tar sand, oil shale and other oil/solids mixtures in accordance to claim 1, characterized by that the oil stripped sand is routed to a heat exchanger for the pre heating of the hot gases to be injected into the plenum of the reactor.

3. A process for simultaneously recovery and cracking/upgrading of oil from solids such as tar sand, oil shale and other oil/solids mixtures in accordance with any of claims 1 and 4, characterized by that the gas is drawn off from the process to be heated by heat exchange in an exhaust heater heated by exhaust from a super heater fuelled by combustion of oil or gas and oil contained in raw oil sand injected into the super heater.

4. A process for simultaneously recovery and cracking/upgrading of oil from solids such as tar sand, oil shale and other oil/solids mixtures in accordance with any of claims 1, 4 and 5, characterized in that the preheated gases from the exhaust heater and the sand heat exchanger is routed to a super heater where it is heated to target temperature by heat exchange from combusted oil or gas and oil contained in raw oil sand injected into the super heater.
Fig. 5

TARBLASTER RESULTS TEST 04.11. AND 05.11.08

1. Raw oil sand
2. Recovered oil
3. Dry clean sand
### A. CLASSIFICATION OF SUBJECT MATTER

IPC: see extra sheet

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)

**IPC:** CIOG

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE, DK, FI, NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

### EPO-INTERNAL, WPI DATA, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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### Date of the actual completion of the international search

8 April 2010

### Date of mailing of the international search report

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International patent classification (IPC)

ClOG 1/02 (2006.01)
ClOB 53/06 (2006.01)

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