

A NEW METHOD OF THE ORGANIC WASTE TREATMENT, CONCERNING WASTE OIL, MIXED PLASTICS WASTE, OIL SLUDGE AND PCBS WASTE PROCESSING WITH SIMULTANEOUS RECOVERY OF HYDROCARBONS

I. Mad'ar¹ and M. Juriga²

¹ Roil Trade s.r.o., Křížna 12, 811 07 Bratislava, SK, ima@blowdec.sk

² Department of Chemical Machines and Equipments, Faculty of Mechanical Engineering, Slovak University of Technology, Nám. Slobody 17, 81231 Bratislava, SK, juriga@sjf.stuba.sk

Abstract. The **BLOWDEC**[®] process is a new and original technology developed from Slovak patent No. 279397. The basic goal is the separation of liquids and solids from the original waste material and the liquefying of the hydrocarbons based polymers by mechanical and thermal degradation of binding forces with simultaneous cracking of heavier hydrocarbons and inhibition of coke formation. The technology is proven for the recycling of waste materials with a high content of organic components, primarily waste mineral oils, oil sludge and waste mixed plastics.

The main principle is the processing of waste organic materials in a hot whirling bed created by solid particles, for example hot sand, in special equipment - the **BLOWDEC**[®] reactor.

The process is also suitable for the treatment of the different types of waste with organic content – refinery sludge, oil-contaminated earth and similar materials polluted with hydrocarbons. During the **BLOWDEC**[®] process, both physical and chemical activities occur, resulting in almost 100% separation (recovery) of the hydrocarbons from waste stream.

Key words: whirling bed of hot solid particles, mechano-activating reactions, separation, cracking, organic waste, waste oil, waste with PCBs content, oil sludge, mixed waste plastics

Introduction

The **BLOWDEC**[®] (**BLOW**ing **DEC**omposition) represents a new and original technology pursuant to the Slovak invention with a granted patent No. **SK 279 397** and following name “*Process for Thermal and/or Catalytic Depolymerisation or Decomposition of Low-grade Organic Substances and Device for Carrying out the Process*”. The patents granted for invention abroad are heretofore as follows: U. S. patent No. US 6,165,349; United Kingdom patent No. GB 233 7265 B; Russian patent RU 218 1126.

The technology taking advantage of the invention has been proved in the course of recycling of waste materials with a high content of organic components, first of all in the course of waste oil recovery and liquefying of waste mixed plastics.

Another application field of the invention that has also been proved is treatment – extraction of oil from hydrocarbon sludges resulting from extraction, transport and treatment of crude oil and utilisation of oil products, as well.

Operational tests have also proved a high effective in the course of elimination of the oils containing PCBs.

Principle of the invention – technical solution

The basic principle of the regeneration process of wastes, low-cost organic substances and destruction of complex com-

pounds of PCBs type, herbicides, pesticides and similar substances consists in their treatment in a hot whirling bed formed by the solid particles, e. g. hot sand, in a special device – the **BLOWDEC**[®] reactor. Simultaneously with the separation of liquid components in the course of treatment of wastes containing liquid or solid hydrocarbons, the cracking of hydrocarbons to an economically attractive product occurs. The chemical reactor pursuant to this invention essentially stands for **novelty** in the technical field of chemical reactors for cracking and separation processes.

The core of the device is a special processing chamber – the **BLOWDEC**[®] reactor. Its construction reminds of a hammer mill and radial air fan, as well. To the basic component parts of the reactor belongs a gas proof cylindrical chamber wherein a rotor to which vanes resistant to friction (ceramic) are attached rotates. The rotor is set in circular motion by motor.

The circular motion of rotor vanes in the reaction chamber brings about an intensive stirring and whirling of the reaction mass consisting of a solid inorganic substance (sand) and an organic component (solid/liquid hydrocarbons). As a result of the friction of rotor vanes against the reaction mass and effect of hydrodynamic forces the heat is generated. The particles of a solid inorganic substance, e. g. sand, form at the same time a fluidised hot whirling bed at the cylindrical face of the chamber (Fig.1).

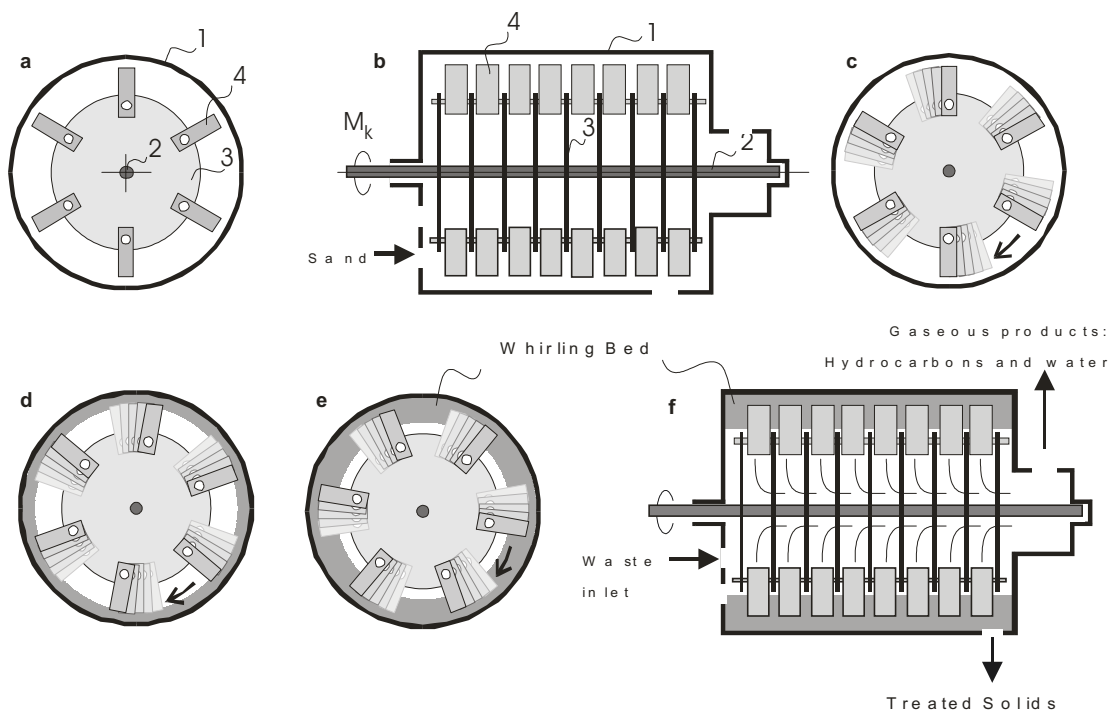


Figure 1 Principle of the process.

- a,b – Basic scheme of the reactor's construction
- c – Start up (movement of the reactor rotor)
- d – Creation of the whirling bed (Sand filling)
- e – Heating of the reactor
- f – Process run

Description: 1- process chamber, 2-shaft, 3-arm of the blade, 4-blade, M_k - torque

An immense quantity of intensively whirling fine solid particles of great kinetic energy has a mechano-activation effect on big hydrocarbon molecules and along with effects of high temperature causes cleaving of molecules. The principal role is also played by a considerable overall surface of the solid particles having an area of some thousand square meters that represents a heat-exchanging surface of high efficiency.

A substantial part of the chemical reactions and physical processes takes place in the whirling bed. The most important chemical reactions going on in a fluidised sand bed are cracking reactions of all types – mechano-activation, thermal and catalytic (SiO_2) ones and their combinations, as well. Primary reaction products of the bigger molecule cleaving enter the recombination and isomerization reactions. Some plastics are a subject to an accidental (polyolefins, PE, PP), other ones to a non random depolymerisation (polystyrene).

An overwhelming part of heavy and solid hydrocarbons crack in light constituents when being in the whirling fluidised sand bed and evaporate simultaneously, then leave the reactor chamber in the form of process gas. At the same time, the substances of lower boiling point (water) evaporate. With regard to that all physical and chemical processes in the course of which the transformation of energy and mass occurs are going on simultaneously in the only one operational stage, the energetic efficiency of the process is very high. Minimally depending on the composition of organic substances entering the **BLOWDEC**® process, the obtained hydrocarbons predominantly do

correspond in their composition to a high-quality energetic (heating) oil with a low or zero sulphur content. With some wastes the process is accompanied by production of light liquid hydrocarbons and hydrocarbon gases as well as by a small production of coke – an elementary carbon which, however, is not deposited in a reactor but in the form of aero dispersion continually taken away by a stream of reaction gas.

The **BLOWDEC**® process results in physical and chemical activities the consequence of which is besides almost 100% hydrocarbon recovery also the change in quality of obtained oil in comparison to original organic substances entering the process. At the same time an effective decomposition of the substances forming the original waste material follows whereby a clean high-quality oil without contaminants is obtained and waste water and solid fragment (in case they were present) wherein the particles of inorganic pollutants, e. g. chlorides in case of PCB treatment are firmly fixed, separated. Oxides of nitrogen and sulphur are not produced.

An important advantage of the **BLOWDEC**® technology is its simple technological equipment and a minimum of devices and apparatuses used (Fig. 2). The very chemical process, as well as the physical treatment of reaction products is computerised. From the economical point of view it is also profitable to run a device of comparatively small production capacity, t. i. device demanding low investment costs. This advantage is multiplied by the fact that one device is able to treat different kinds of wastes of different composition.

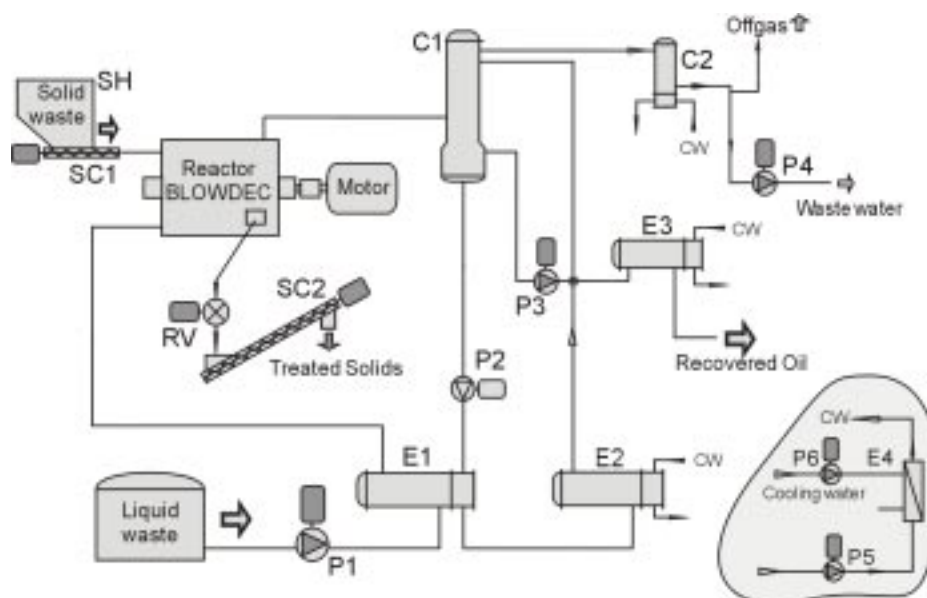


Figure 2. Simplify flow chart. SH - Solid hopper, SC1~2 Screw conveyer, RV- Rotary valve, P1~6 - Pumps, C1- quench condenser, C2- plate condenser, E1~E3 heat exchanger, CW- Cooling water.

Experimental Station - Operational Experience

The first industrial technological **BLOWDEC**[®] unit with a proposed capacity to treat 3500 tons waste oil a year and a 200 kW reactor is currently being installed by a recycling factory of an important waste oil processor in Slovakia – KONZEKO Ltd. Markusovce. The unit was built up with the assistance of a grant by EU - PHARE fund.

The construction of a 200 kW reactor (thermal resistance) and an overall arrangement of the first unit do not enable to verify all the prospective fields of application, therefore in the course of 2002 the second “research and development“ **BLOWDEC**[®] unit with a 45 kW reactor was built up in the vicinity of Bratislava and set in probation running in January 2003. The

testing of different kinds of real and “simulated“ waste materials have been carried out in here in the first stage.

The tests have proved that it is possible to treat all the kinds of wastes taken into consideration under economically favourable conditions and obtain valuable, from the commercial viewpoint attractive, energetic oil and a hydrocarbon gas. Also the waste mineral oils, oil - crude oil sludge, clean and waste mixed plastics have been tested.

The testing of elimination of transformer oils containing dangerous PCBs (polychlorinated biphenyls) currently being exported out of Slovakia for their liquidation has proved that it is even possible by means of the **BLOWDEC**[®] process to successfully and economically eliminate such kinds of dangerous persistent organic substances.

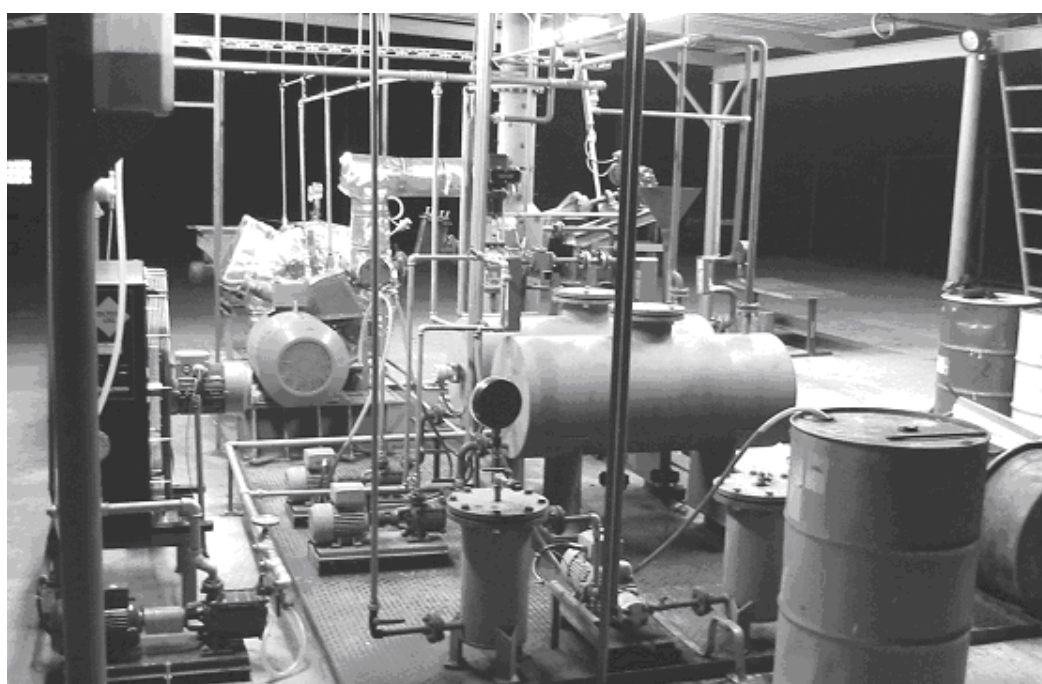


Figure 3. General view to experimental station (Kuchyňa, Slovakia).

Results of the Experiments.

The testing program applicable to several raw material resources has proved that it is possible to qualify the final products as a light heating oil with a low or zero sulphur content. The results of a research in progress aimed at optimum utilisation of obtained hydrocarbons as semi finished products for more refined, e. g. petrochemical treatment seem to be prospective.

A side product in the process of oil sludge treatment is a very finely ground inorganic solid fragment containing traces of hydrocarbons. By means of this product it is possible to replace in an advantageous way an important constituent in production of road asphalts – so called filler currently replaced by e.g. finely ground calcite.

The PCBs elimination is characterized by a high conversion whereby a substantial part of chlorine is by means of the process bound in chlorides (sodium and calcium) forming a part of a solid fragment extracted from process.

Waste oil treatment. The EU uses annually approx. 5 mill. tonnes of oil [6] arising as a waste product of the use of oils in a wide range of industrial and commercial activities, such as engineering, power generation and vehicle maintenance, of which approx. 2,5 mill. tonnes are recollected, this is cleaned and recycled mostly as heavy heating oil. During use in machines the oil and pollutants become a stable dispersion system composed of the hydrocarbon phase of the original oil, solid particles and water. An adverse feature of such dispersion is its stability and acceptable physical separation of components cannot be practically implemented.

The basic goal during the waste oil treatment is the destruction of additives and their residuals which are responsible for stability of the dispersion by mechanical and thermal degradation and a simultaneous inhibition of coke formation.

Additives added to oil are mostly heterogeneous organic materials, containing, in addition to carbon and hydrogen atoms, zinc, phosphorus, calcium, nitrogen, oxygen, etc. Such materials have a limited heat resistance, which offers a method for their removal. Technologies operating on the principle of thermal destruction of additives are well known world-wide, but not as yet broadly applied. The most frequently used principle is delay coking, a version of thermal cracking, which produces gas oil and coke. The BLOWDEC technology is competitive alternative for waste oil processing. The distribution of additives elements (Tab.1) demonstrates efficiency of the BLOWDEC process for waste black oil treatment executed at the tem-

perature of about 370°C.

The quality liquid fuel and base lubricating oil can be obtained from the regenerated oil by the fractionation of the raw recovered oil via distillation e.g. in the molecular vacuum thin film evaporator (Tab.2).

Oil with PCBs treatment. PCBs (polychlorinated biphenyls) are considered due to their toxicity and persistence as very dangerous chemicals that come in various forms including oily liquids, solids and hard resins. PCBs are organochlorines that were manufactured until the mid-1980s. They are still found in old electrical equipment. PCBs are very persistent in the environment, taking years to degrade. All PCBs from Slovakia are exported for disposal abroad, while there is no suitable technology for destruction of such waste stream. The test (Tab.3) during which hot whirling bed of solids was created with strong alkalic agent showed that at the temperature of about 500°C could be PCBs oil successfully eliminate.

The oil sludge treatment. The US petroleum-refining industry annually produces more than 2,5 million tonnes of wet hazardous oil sludge, and in addition large quantities of non-hazardous sludge from crude, refined products and intermediate product tank bottoms. Similar sludge (artificially prepared from the waste oil, water and the soil) was treated in the BLOWDEC® unit at the temperate of 390°C. Summary of this test run are in Table 4.

Mixed waste plastics treatment. The total amount of plastic wastes generated by our society is growing rapidly. The main source of plastic waste in Western Europe (18,5 mill. tons/year) is the municipal solid wastes (MSW) (63,5 wt.%) followed by distribution and large industry (19,5wt.%) [7]. Plastic consumption is increasing by 4% each year. If this trend continues, we will soon be swamped by waste plastics. There is a commonly held view that not all plastics can be recycled. That is not true. All plastics can be reused, recycled, or have energy recovered from them. One of the possible ways was proved in BLOWDEC test unit. The artificially prepared plastics mix was processed at the temperature of 430°C and turned to liquid and gaseous hydrocarbon product (Tab. 5).

Industrial applicability of the BLOWDEC® technology

It is possible to apply the BLOWDEC® process and technology as an advantageous alternative to already known technologies in several fields. There have been no known econom-

Table 1. Additives elements (typical) distribution during the waste black oil „cocktail“ treatment in the BLOWDEC® process

Oil type	SAE 10W-40	SAE 10W-40	Waste black oil "cocktail"	BLOWDEC	Ash from sediment
Elements	Fresh (ppm)	Waste (ppm)	content in oil part (ppm)	regenerated oil (ppm)	(% wt.)
Zink (Zn)	879	625	319	2,3	0,41
Calcium (Ca)	1520	1180	833	2,6	3,19
Phosphorus (P)	680	450	350	0,0014	0,56
Water content & light HC			10,8 % wt.		
Ash contents					12,71

Table 2. Properties of distillation fractions from the product of the waste black oil regeneration in process BLOWDEC® fractionated in short way vacuum film evaporator

		Raw Recovered Oil	Distillate No.1 yield 18,5% Bearing oil	Distillate No.2 yield 72,9% NS 150
Parameter	Unit	Value	Value	Value
Density at 20°C	kg/m ³	874	865	878
Viscosity at 40°C	mm ² /s	29,1	—	—
Viscosity at 20°C	mm ² /s	—	5,90	42,4
Viscosity at 100°C	mm ² /s	—	—	6,2
VI (Viscosity index)	—	—	—	95
Diesel index	—	61	48,7	—
Distillation test	—	—	—	—
Initial boiling point	°C	65	224	—
up 250°C recovered	% vol.	7	9	—
up 350°C recovered	% vol.	25	55	—
up 360°C recovered	% vol.	36	70	—
End of distillation / recovered	°C / % vol.	385 / 50	385 / 99	—
Sulphur content	% wt.	0,32	0,246	0,51
Pour point	°C	—	-14	—
Freezing point	°C	-20	-29	-18
Flash point (PM)	°C	<20	109	210
Acid number	mg KOH / g	2,6	0,10	0,07
Determination of ash	% wt.	—	0,001	0,001
Conradson Carb. Residue - 10%	% wt.	—	0,015	0,054
Corrosion Cu 3h/100°C	—	—	—	1a
Corrosion Fe 3h/100°C	—	—	—	negat.
Resins content	% wt.	—	—	0,53
Colour ISO	—	—	—	4,5
Colour after clay bleaching (5%, 200°C, N ₂)	—	—	—	3,0
Appearance	—	—	—	B&C
Acid number	% wt.	0,03	—	—
Conradson Carbon Residue	% wt.	0,05	—	—
Aniline point	°C	91,1	—	—
Bromium number	g Br/100g	15	—	—
Average molecular weight	—	312	—	—
Aromatic carbon content	%	13	—	—
IR method				
Paraffin carbon content	%	61	—	—
IR method				

Table 3. Results of the PCBs in insulation oil destruction test

Material	Waste transformer oil with PCBs	Oil after the treatment (ppm)	Solids after treatment (ppm)
Parameter			
Total organic chlorine	3,1% wt.	1048	2,6
PCB content	2790 ppm	1,3	3,2
Chlorides	—	—	5990

Table 4. Results of the oil sludge treatment in the BLOWDEC® process

Material Content	Oil sludge (% wt.)	Separated solids	Recovered oil (% wt.)
Hydrocarbons (oil)	18,5	840 ppm	99,8
Solids	75	99,9 % wt.	0,12
Water	6,5	0,1 % wt.	0,08

Table 5. Results of the mixed plastics treatment in the BLOWDEC® process

Reference composition of the mixed plastics		Properties of the liquefied oil recovered by the reference mixed plastics conversion at 450°C		
Component	Value (% wt.)	Parameter	Unit	Value
HD PE	10	Density at 20°C	kg/m ³	881
LD PE	38	Viscosity - 40°C	mm ² /s	29,1
PP	30	Mechanical impurities	% wt.	0,14
PS	15	Water content	% wt.	0,05
PA	4	Sulphur content	ppm	25
PMMA	1	Pour point	°C	8
PUR	2	Calorific value	MJ/kg	41,8
PVC (!)	0	Distillation test: up 350°C recover.	% vol.	26

ically accepted processing technologies (mixed plastics) in the world yet in some fields of process utilisation. Very promising is its application in the sphere of upgrading of the alternative raw material resources (coal conversion, bitumen sands, and deserted oil fields).

The two main areas of application of the BLOWDEC® technology are as follows:

- WASTE MANAGEMENT
- UPGRADING OF HEAVY HYDROCARBONS

WASTE MANAGEMENT – treatment of wastes containing petroleum substances represents a field the process was developed for. A characteristic feature is a high adaptability to the composition of incoming waste materials.

A majority of wastes containing hydrocarbons produced in the course of oil exploitation, transport and treatment as well as when making use of petroleum products represents a mixture of oil – water – solid substance. The individual kinds of wastes only differ in different proportion of individual components and in stability of disperse system the nature of which is often typical of waste. Out of a huge spectrum of such wastes, an extreme example can be given by the waste motor oil on the one hand and dewatered oil sludge from the refinery waste-water treatment plant on the other hand. It is possible to successfully treat both kinds of wastes by means of the BLOWDEC® process and at the same time get the oil back. Since there is also the cracking of the present hydrocarbons in the course of process, the oil obtained in such way is of attractive economic value.

A prospective and proved field of application of the BLOWDEC® technology within “waste management“ is treatment of waste plastics, first of all polyolefins (PE, PP), polystyrene (PS) and other widespread plastics.

THE HEAVY HYDROCARBON CRACKING represents another attractive area of application of the BLOWDEC® technology. Cleaving – cracking of the heavy oil fractions is a common way of depth oil treatment. The raw materials used for BLOWDEC® are heavy residues of atmospheric and vacuum distillation of crude oil or its chemical treatment.

The utilization of alternative raw material resources such as heavy crude oils (Kazakhstan), oil-bearing shales and sands (Athabaska, Canada) or natural bitumens (Trinidad, South America) represents a promising future field of application of the BLOWDEC® technology. The already known technologies enable upgrading of vast fields of such hydrocarbons to

a sufficient economic effect, however, the application of the BLOWDEC® process can make these hydrocarbon resources much more attractive. Another possible application field consists in reopening of oil exploitation on deserted oil fields where the oil exploitation was brought to a halt because of a high sand content in oil.

Final remarks - benefits of the process

The BLOWDEC® technology has many significant benefits and it enables:

- effective, almost 100% recovery of hydrocarbons from wastes containing petroleum substances such as waste mineral oils, refinery sludges and sediments, sludge from oil exploitation and transport, tar sludges
- economical conversion of separated as well as waste mixed plastics to liquid hydrocarbons
- extraction of hydrocarbons from alternative sources such as oil and tar sands, natural bitumens, crude oil with a high sand content
- simple and effective elimination of wastes containing PCB and other troublesome persistent organic substances
- flexibility to waste composition and treatment of wastes, raw material resources within a single working stage independently of a contamination level or composition of an incoming stream
- lack of coke residues formation in a device
- low specific power consumption or high energetic effectiveness in comparison to other technologies
- ecological operation without formation of dangerous wastes and gaseous emissions – sulphur and nitrogen oxides
- compact unit with a comparatively simple technological device demanding little room
- low investment resources requirement.

Reference

- [1] Slovak patent No. 279 397
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