3rd World Congress on Petrochemistry and Chemical Engineering November 30-December 02, 2015 Atlanta, USA

Institute of Combustion Problems

PROCESSING OF HEAVY OILS AND OIL SANDS

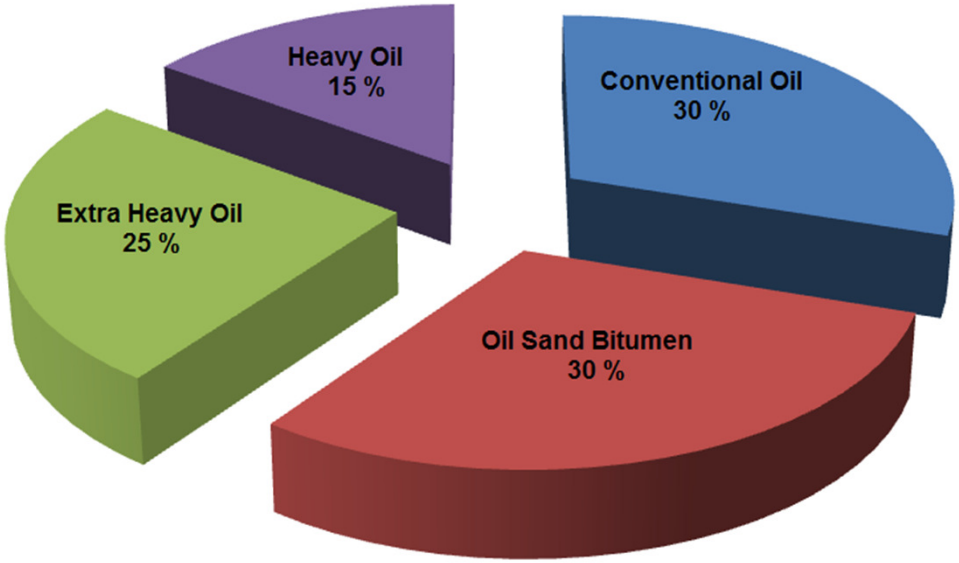
Prof. Z.A. Mansurov

1 December, 2015

OUTLINE

- Introduction;
- Oil sands of Kazakhstan deposits;
- Problems of processing of oil sands;
- Obtaining of synthetic oils;
- Ultrasonic methods for separation of organic and mineral parts;
- Composites with rubber crumb;
- Bio-remediation of oil-contaminated soils.

Total world oil reserves



Conventional oil is a mixture of mainly pentanes and heavier hydrocarbons.

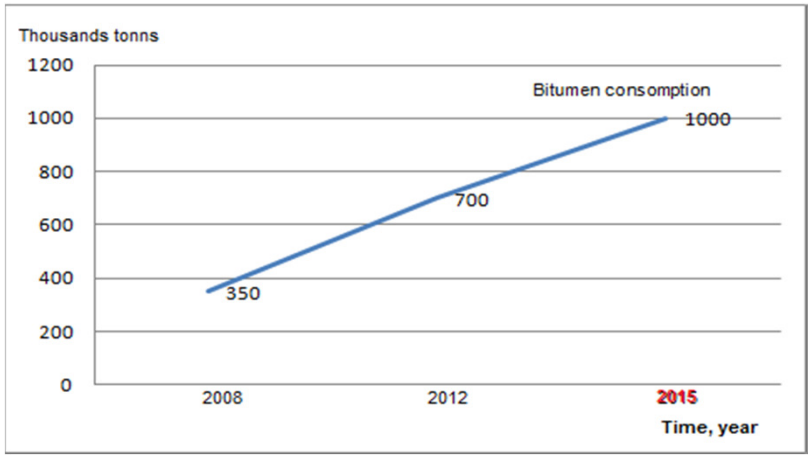
Unconventional oil is petroleum produced or extracted using techniques other than the conventional (oil well) method. Unconventional oil included extra-heavy oil, oil sands, kerogen oil, shale oil. It is in semi-solid form mixed with sand and water, as in the Athabasca oil sands in Canada

Heavy crude oil is oil that is highly viscous, and cannot easily flow to production wells under normal reservoir conditions. It is referred to as "heavy" because its density or specific gravity is higher than that of light crude oil.

Extra heavy crude oil is oil that is highly viscous, and cannot easily flow to production wells under normal reservoir conditions, too. Venezuela has large amounts of oil in the Orinoco oil sands, although the hydrocarbons trapped in them are more fluid than in Canada and are usually called extra heavy oil.

ACTUALITY OF RESEARCH

- At present oil producing sector has a leading position in the structure of national economy of Kazakhstan.
- Over 50 fields of oil sands (oil-bituminous sands, tar sands, extra heavy oil) have been discovered in Kazakhstan. Canada and Venezuela are currently the most successful producer for unconventional oil production.
- Oil bitumen are widely used in many industries, therefore their production is the important economic problem and requires constant perfection.
- The main problem with road building is the poor quality of bitumen used in asphalt-concrete pavements.



Graphic of bitumen consumption



Oil sands in Kazakhstan

Oil sand of Western Kazakhstan

Oil sands – is fossil fuels, an organic part of which represents a natural bitumen (NB).
The reserves of the oil sand in the Western Kazakhstan is very significant and attract them as a valuable material for road construction, the pace is increasing, It is an urgent task, a decision which will reduce the cost road construction in general.

Object and Purpose of the research

- **Production of Rubber-Bitumen Compounds**

based on rubber crumb from worn tires

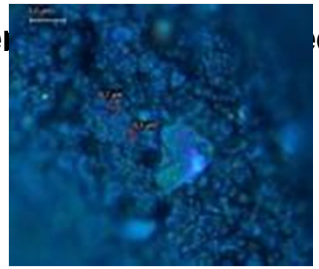




BND 60/90 paving bitumen

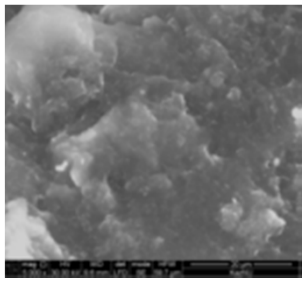
Rubber crumb: (from Kazakhstan Rubber Recycling LLP)

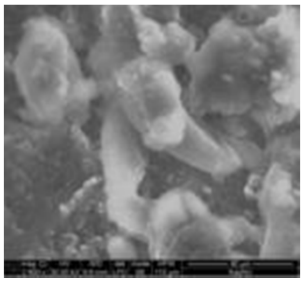
Spe d m





Optical microscope images of rubber crumb





SEM images of rubber crumb



Microwaves and radio frequency applications in oil sands of Canada

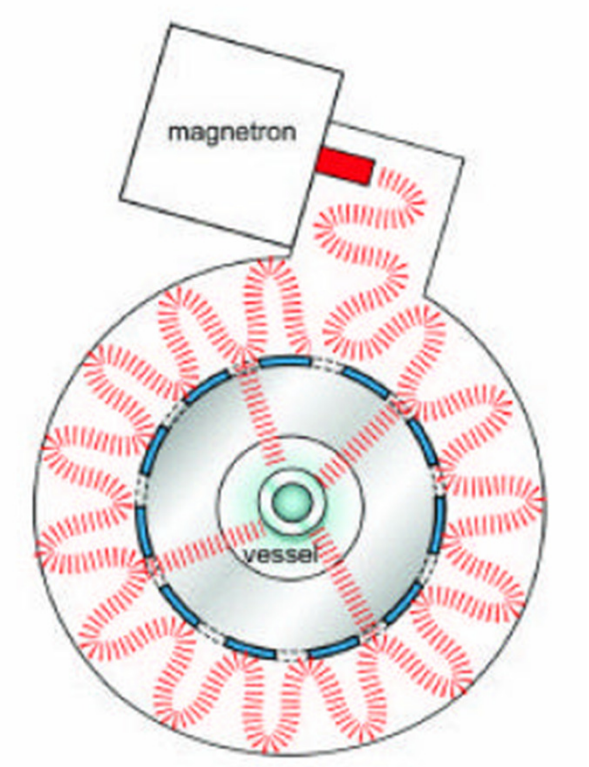
There are 1.7 trillion barrels of bitumen in place in Canadian oil sands and the resource will become a major source of petroleum products in the near future. Extra heavy oil has been commercially produced from Alberta's massive oil sands resources for four decades. Through the evolution of technology, the efficiency and performance of oil sands extraction, separation and upgrading technology has advanced, while operating costs have fallen. In 2005, Alberta produced more than 1 million barrels per day of upgraded crude oil and bitumen from oil sands, and projections are that over three million barrels per day could be produced in 2030.

The evolution of Alberta's oil sands industry contributes both technology and lessons learned to guide further development of North America's heavy oil resources.

In 2003, samples of Lloydminster oil sands (oil–water–solids ratio of 19: 40: 41) considered particularly stubborn to separation were tested with exposure to variable frequency microwaves.

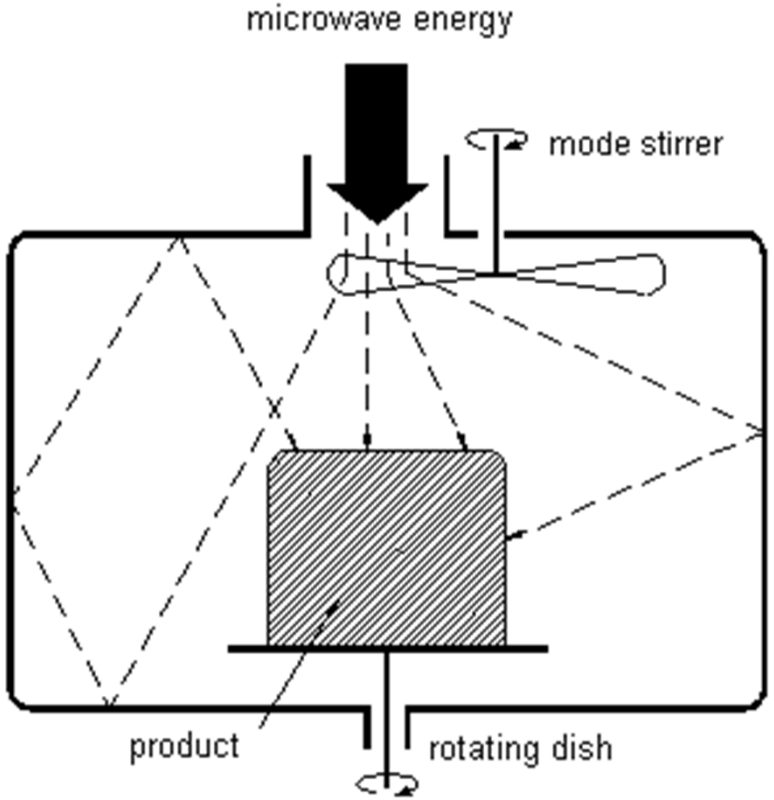
Sateesh Mutyala et. al. Microwave applications to oil sands and petroleum: A review. Fuel Processing Technology. 91. (2010). 127–135.

Microwave Chemistry Apparatus



Single-mode Heating Apparatus[1]

The factor that governs the design of a single-mode apparatus is the distance of the sample from the magnetron. This distance should be appropriate to ensure that the sample is placed at the antinodes of the standing electromagnetic wave pattern



Multi-mode Heating Apparatus[2]

An essential feature of a multi-mode apparatus is the deliberate avoidance of generating a standing wave pattern inside it.

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1. *Self-turning Single-mode cavity in DiscovererTM system by CEM Corporation*
2. http://www.pueschner.com/engl/basics/index.html

STUDY AND PROCESSING OF OIL SANDS

Characteristics of solvents

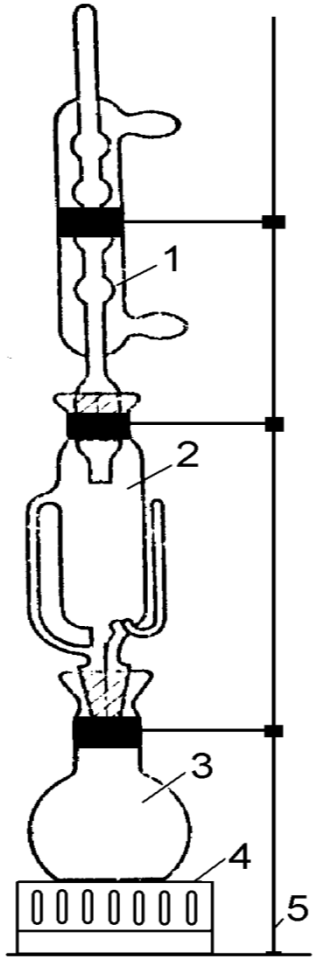
№	Solvents	Molecular formula	Boiling point, ^{0}C
1	Hexane	C_6H_{14}	69
2	Toluene	C_7H_8	111
3	Benzene	C_6H_6	80.1
4	Ethanol	C_2H_6O	78.37

Physical and chemical properties of natural bitumen

Oil sand samples	Characteristics	NB extracted by hexane	NB extracted by toluene	NB extracted by the ethanol and benzene mixture
Munayli-Mola OS	Organic part, wt%	15.5	16.5	15.9
	Density, g/cm^3	0.997	1.090	0.987
	Heating value, j/g	43006	42464	41857
Beke OS	Organic part, wt%	10.6	11.3	11.2
	Density, g/cm^3	0.917	0.925	1.002
	Heating value, j/g	42728	43264	42536

Comparison results of ash content determination and extraction

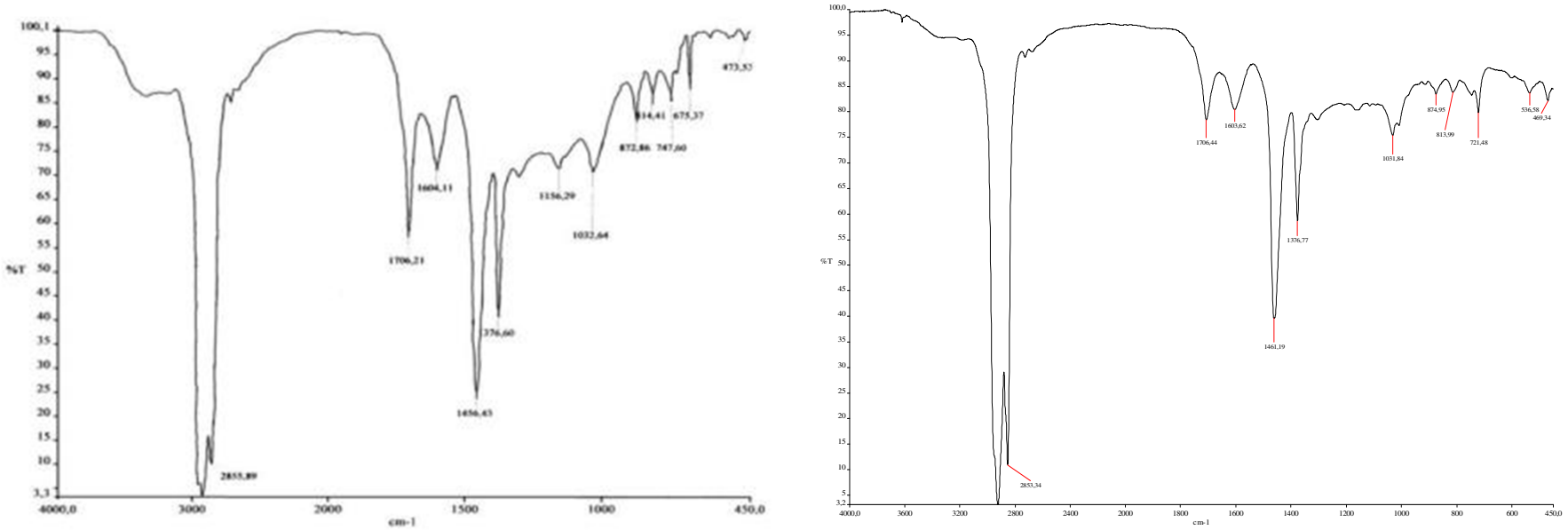
Research object	Methods	Contents	
Munayli-Mola oil sands	Extraction method	Extracted oil, wt. %	After extracted sands, wt. %
		16	84
	Determination of ash content	Organic part, wt. %	Ash content, wt. %
		16.7	83.3



1-reflux condenser, Soxhlet apparatus 3-flask, 4- heating plate, 5-upright

Elemental composition of bitumens

Type of bitumen		Ash content. wt. %	Content, wt. %				
			C	H	S	N	O
Munayli-Mola oil sands	Natural bitumen extracted by hexane	0.082	84.36	12.16	1.294	0.29	1.814
	Natural bitumen extracted by toluene	1.3	85.00	12.34	1.010	0.30	0.15
	Natural bitumen extracted by ethanol/benzene	0.13	84.69	11.39	1.292	0.38	2.118
Standard paving bitumen BND 60/90		0.167	84.91	11.01	3.050	0.52	0.343
Beke oil sands	Natural bitumen extracted by hexane	1.02	85.25	11.54	0.436	0.44	1.214
	Natural bitumen extracted by toluene	1.17	84.49	11.39	0.482	0.47	1.998

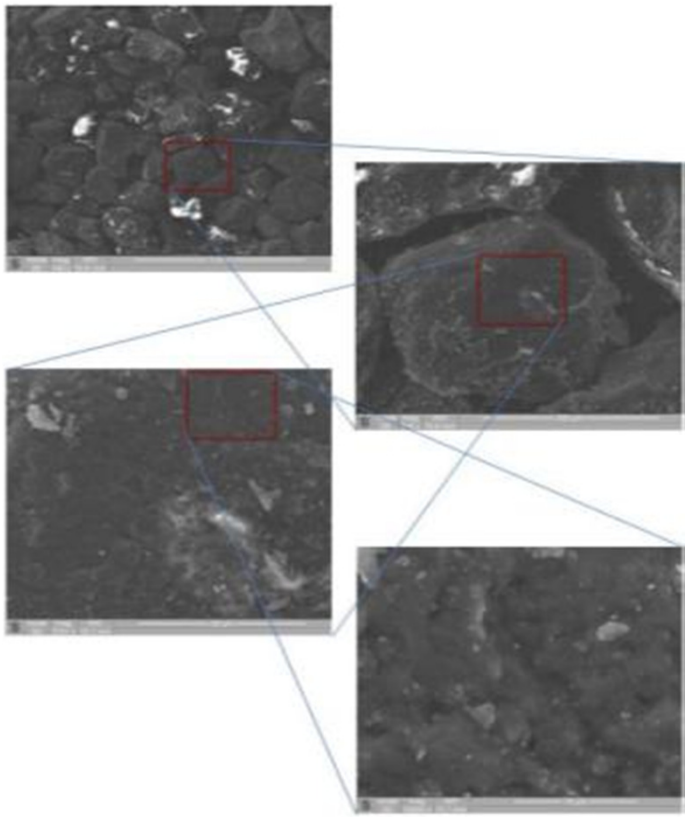


IR spectrum of natural bitumen

MINERAL PART OF OIL SANDS

Oil sand's mineral composition

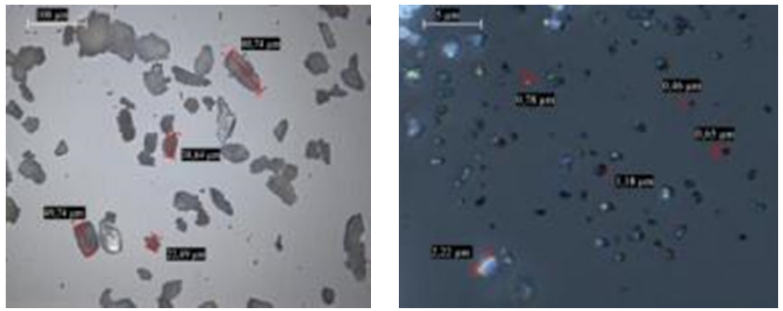
Sample	Name of the composition	Chemical formula	Content, %
Mineral aggregates of Munayli-Mola OS after extracted by hexane	Quartz	SiO_2	79.1
	Albite	$NaAlSi_3O_8$	11.8
	Microcline	$KAlSi_3O_8$	9.0
	Footprints of carbon	C	0.1
	Total		100
Mineral aggregates of Munayli-Mola OS after extracted by toluene	Quartz	SiO_2	72.1
	Albite	$NaAlSi_3O_8$	14.1
	Microcline	$KAlSi_3O_8$	13.8
	Footprints of carbon	C	0
	Total		100
Mineral aggregates of Munayli-Mola OS after extracted by B/E mixture	Quartz	SiO_2	75.5
	Albite	$NaAlSi_3O_8$	11.2
	Microcline	$KAlSi_3O_8$	13.3
	Footprints of carbon	C	0
	Total		100



SEM image of oil sand's mineral part

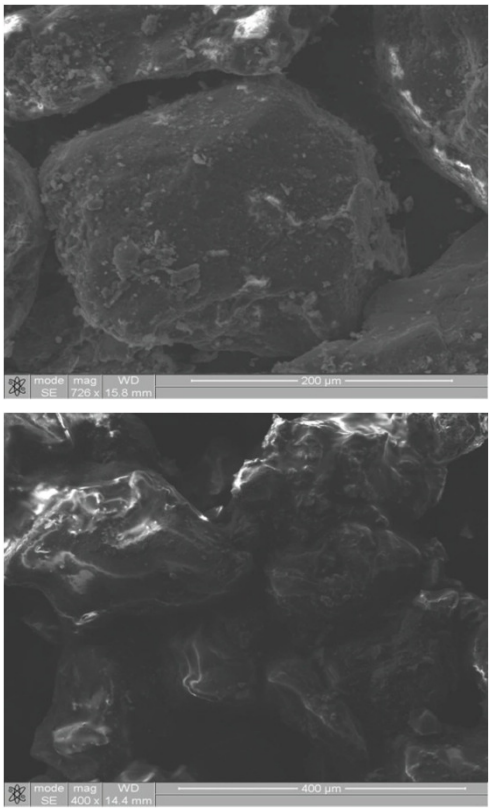
Elemental composition of clay minerals of oil sand

Element	Concentration, %	Intensity, cps
Fe	0.349	3.95
K	1.270	2.26
Ca	60.304	255.13
S	29.799	17.78
Cl_2	3.987	2.24
P	3.773	1.09
Sr	0.329	3.85
Mn	0.189	1.58

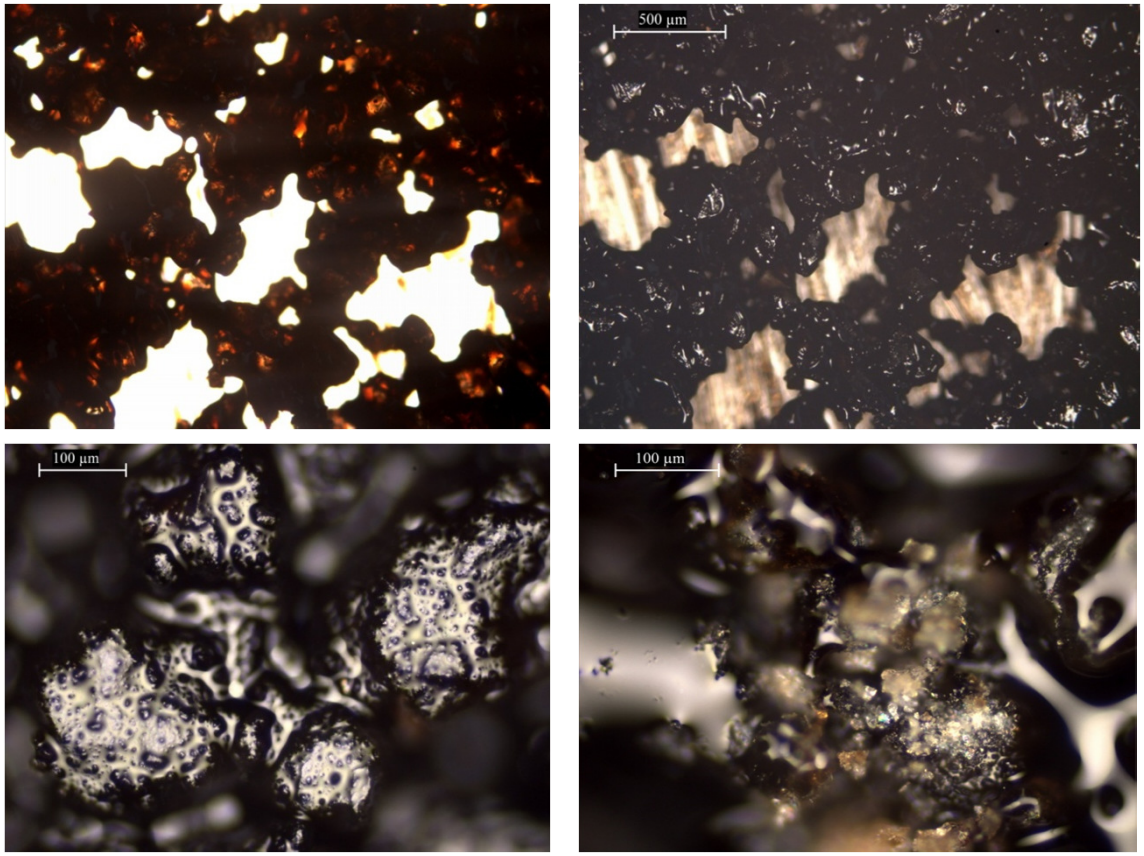


Optical microscopic image of clay mineral composition

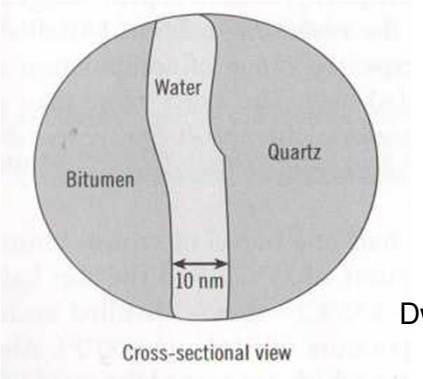
MICROSCOPIC STUDY OF OIL SAND STRUCTURE



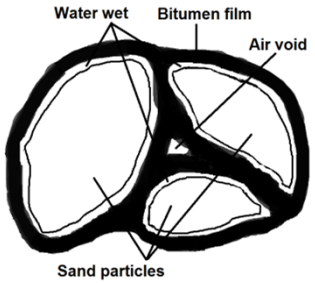
SEM image of oil sand



Optical microscopic images of Beke oil sands



Dwijen K. Banerjee , 2012



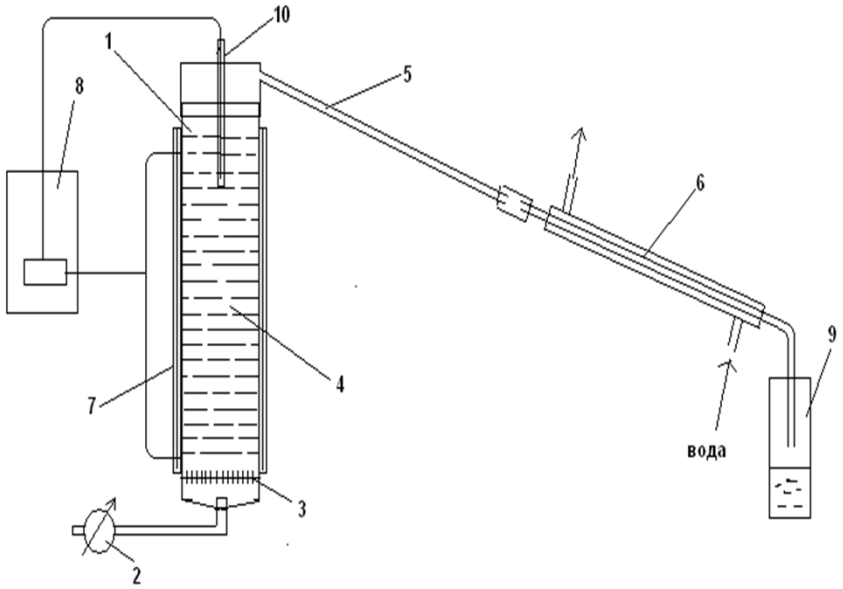
THERMAL PROCESSING OF OIL SANDS

Thermal processing products of Beke oil sand

Parameters	Contents
Yield of products, wt. %	
Gaseous	2.4
Liquid	9.6
Solid residue	88.0
Characteristics of the liquid fraction:	
Density, g/cm^3	0.862
Ash, %	0.38
Flash point, °C	42
Fractional composition, wt. %:	
Boiling point – 180 °C	19.6
180-250 °C	24.0
250-350 °C	33.0
350- end of boiling	23.4

Thermal processing products of Munayli-Mola oil sand

Parameters	Contents
Yield of products, wt. %	
Gaseous	1.5
Liquid	13.5
Solid residue	85
Fractional composition, wt. %:	
Boiling point – 180 °C	6.1
180-250 °C	15.1
250-350 °C	46.8
350- end of boiling	28.8



Scheme of apparatus for the thermal processing oil sands
1 – cylindrical reactor, 2 – tube, 3 – Perforated diaphragm, 4 – raw material, 5 – connecting pipe for output gas and products, 6 – refrigerator, 7 – electric furnace, 8 – thermoregulator, 9 – receptacle.

CHARACTERISTICS OF SYNTHETIC OIL PRODUCED FROM BEKE BITUMEN

Parameters	The initial sample	Gasoline fraction 80-180 °C	Diesel fraction 180-250 °C	Gasoil fraction 250-320 °C
Octane number	-	80	not defined	not defined
Cetane number	-	-	above 45	not defined
Flash, °C	-	-	35-40	-
Density at 20 °C, kg/m^3	0,870	0,754	0.817	0.864
Pour point, °C	-40	not defined	-50-55	-45
Filterability temperature limit, °C	above -35-40	not defined	above -40	above -25
Benzene volume, %	-	1	not defined	not defined





Pilot installation for thermal processing of oil sands

VACUUM DISTILLATION OF HYDROGENATED OIL

Characteristics	Oil fractions at		
	I.B. – 215 °C	216 – 316 °C	316 °C – E.B.
Pressure, mbar	808	805 - 60	60 -
Mass of fraction, g	80.39	72.72	43.88
Yield of fraction, %	40.81	36.91	22.27

Characteristics	1st fractions	2nd fractions	Vacuum residue
Temperature, °C	Initial boiling point - 215	216 - 316	316 -
Pressure, mbar	808	805 - 60	60 -
Mass of fractions, g	24.64	85.78	77.37
Yield of fractions, %	13.12	45.68	41.20

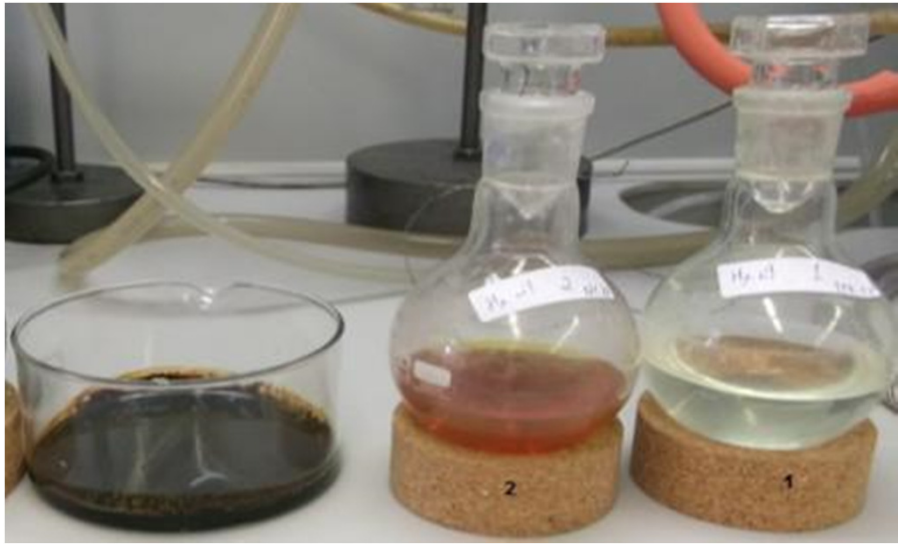


Image of vacuum distillation products

1 – 1st fraction, 2 – 2nd fraction, Without number – Vacuum residue

DENSITY AND ASH CONTENT

Characteristics\ samples	Natural bitumen	Hydrogenated oil
Density, g/cm3	0.921	0.89
Medium ash content, wt. %	1.1	0.2

PRODUCTION OF OXIDIZED BITUMEN FROM NATURAL BITUMEN OF BEKE OIL SAND

Physical and mechanical characteristics of bitumens, obtained at a temperature of 230 °C

Name of the indicators	Sample № 1	BND 90/130	Sample 2	BND 40/60	Sample № 3
Penetration at 25 °C, 0,1 mm	115	91-130	46	40-60	30
Softening point, °C	44	not less than 43	52	not less than 51	65
Ductility, cm	76	at least 65	45	at least 45	8
Flash point, °C	237	not less than 230	235	not less than 230	220

Physical and mechanical characteristics of bitumens, obtained at a temperature of 240 °C

Name of the indicators	Sample № 1	BND 60/90	Sample № 2	BND 40/60	Sample № 3	BN 70/30
Penetration at 25 °C, 0,1 mm	62	61-90	43	40-60	29	21-40
Softening point, °C	53	not less than 47	61	not less than 51	70	70-80
Ductility, cm	64	at least 55	31	at least 45	12	at least 3.0
Brittle point, °C	-16	not more than -15	-10	not more than -12	-	-
Flash point, °C	225	230	232	230	239	not less than 240

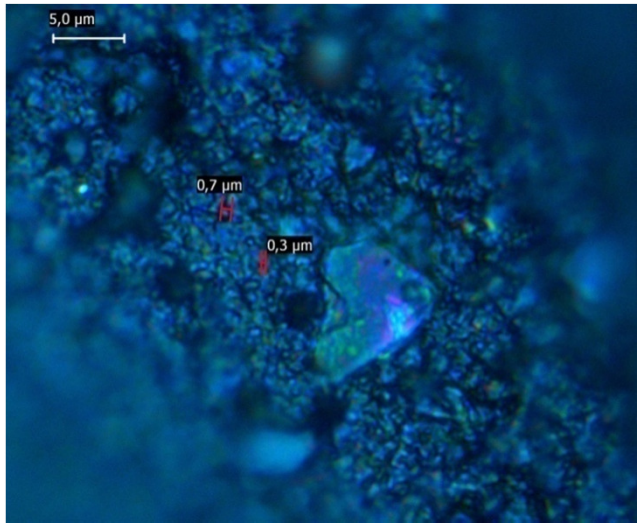
Physical and mechanical characteristics of bitumens, obtained at a temperature of 270 °C

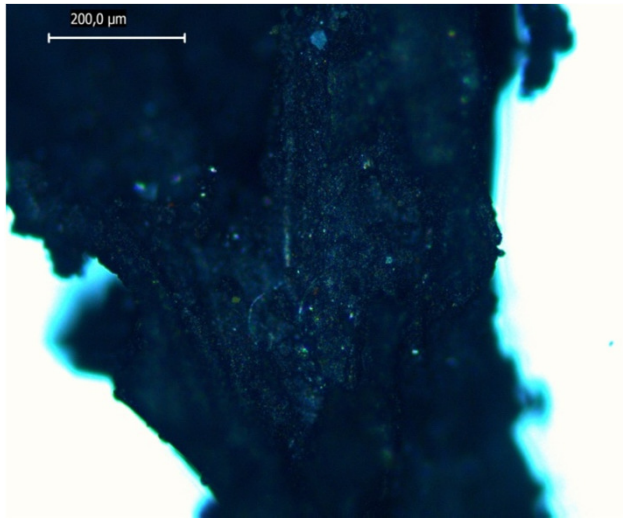
Name of the indicators	Sample № 1	BD 70/30	Sample № 2	BD 90/10	Sample № 3
Penetration at 25 °C, 0.1 mm	32	21-40	12	5-20	7
Softening point, °C	72	70-80	85	90-105	92
Ductility, cm	18	at least 3.0	4.0	at least 1.0	2.1
Flash point, °C	238	not less than 240	235	not less than 240	-

PREPARATION OF ASPHALT CONCRETE WITH OIL SANDS

Name of indicators	Content of oil sands in asphalt mix			Basic requirements for the ST RK 1225-2003
	28 %	47 %	60 %	
Medium density, g/cm^3	2.29	2.30	2.22	not rated
Water saturation, %	6.1	2.4	2.6	for the dense type of B, V, G from 1.5 to 4.0 for the porous type from 5 to 10
Compression strength, MPa, at 20 °C	8.7	4.6	4.2	not less than 2.5 for M1 not less than 2.2 for M2 not less than 2.0 for M3
Compression strength, MPa, at 20 °C water-saturated	6.5	4.7	4.8	not rated
Compression strength, MPa, at 50 °C	2.1	1.1	0.6	not less than 1.3 for B M1 not less than 1.2 for B M2 not less than 1.1 for B M3 not less than 0.7 for the porous M1 not less than 0.5 for the porous M2
Compression strength, MPa, at 0 °C	14.9	13.0	5.1	no more than 13.0 for the porous not rated
Water resistance	1.0	0.75	0.64	not less than 0.85 for the dense M1 not less than 0.80 for the dense M2 not less than 0.7 for the porous M1 not less than 0.6 for the porous M2
Water resistance with prolonged water saturation	0.55	0.78	*0.43*	not less than 0.75 for the dense M1 not less than 0.7 for the dense M2 not less than 0.6 for the porous M1 not less than 0.5 for the porous M2
Adhesion of binder to the mineral portion of the mixture	-	-	-	braves (at least ¾ surface of the mixture covered with foil binder)

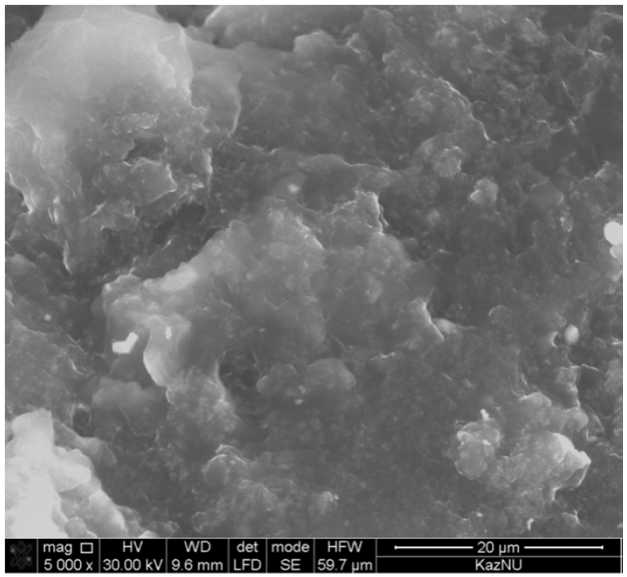
PRODUCTION OF RUBBER BITUMEN COMPOSITION MATERIALS

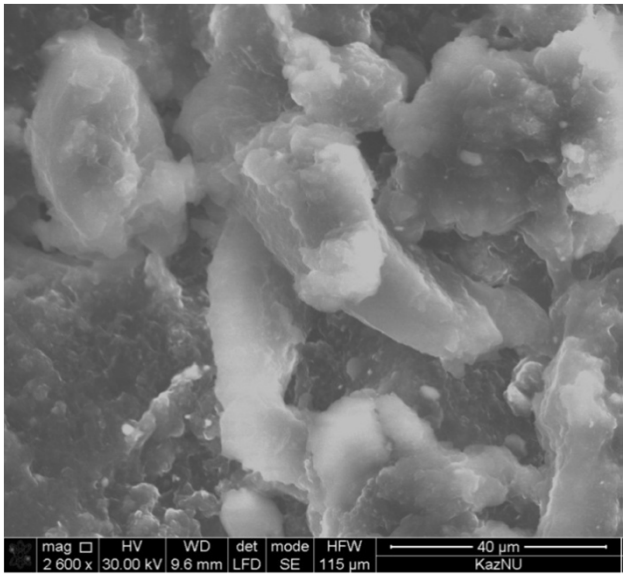




Optical microscope images of rubber crumb

SEM images of rubber crumb





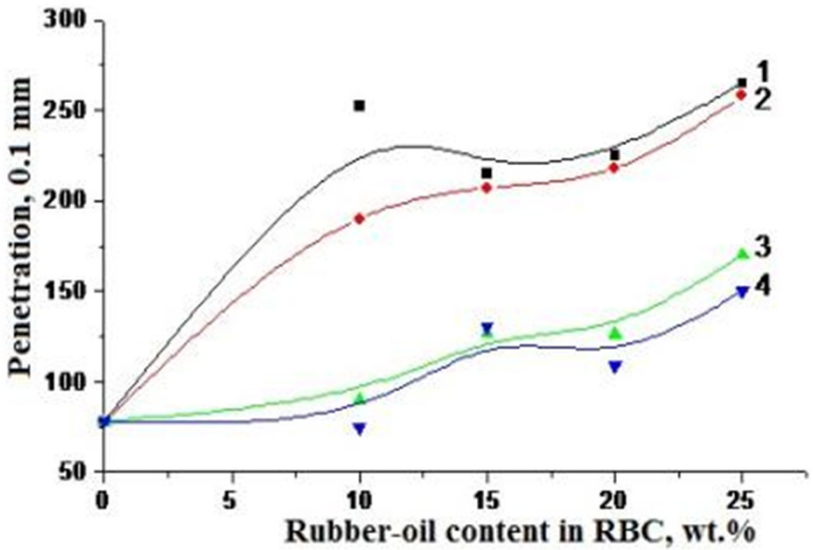
Physical and mechanical characteristics of RBC with rubber crumb (less than 0.6 mm)

Name of indicators	Rubber-oil ratio	Rubber-oil percentage in bitumen				Methods of testing
		10 wt%	15 wt%	20 wt%	25 wt%	
Penetration at 25 °C, 0.1mm	R:O=1:1	90	127	126	170	According to standard 11501
	R:O=3:2	75	130	109	150	
Softening point, °C	R:O=1:1	51	46	50	48	According to standard 11506
	R:O=3:2	58	47	55	46	
Ductility at 25 °C, cm	R:O=1:1	25	19	26,5	22	According to standard 11505
	R:O=3:2	19	31	17	25	
Penetration index	R:O=1:1	0.6	0.3	1.5	2.2	By empirical formula
	R:O=3:2	1.7	0.7	2.2	0.9	
Changing of softening temperature after heated, °C	R:O=1:1	5	5	5	5	According to standard 18180
	R:O=3:2	4	5	5	6	
Standard accordance	R:O=1:1	–	–	RBC 90/130	RBC 130/200	According to R RK 218-76-2008
	R:O=3:2	RBC 60/90	–	RBC 90/130	RBC 130/200	

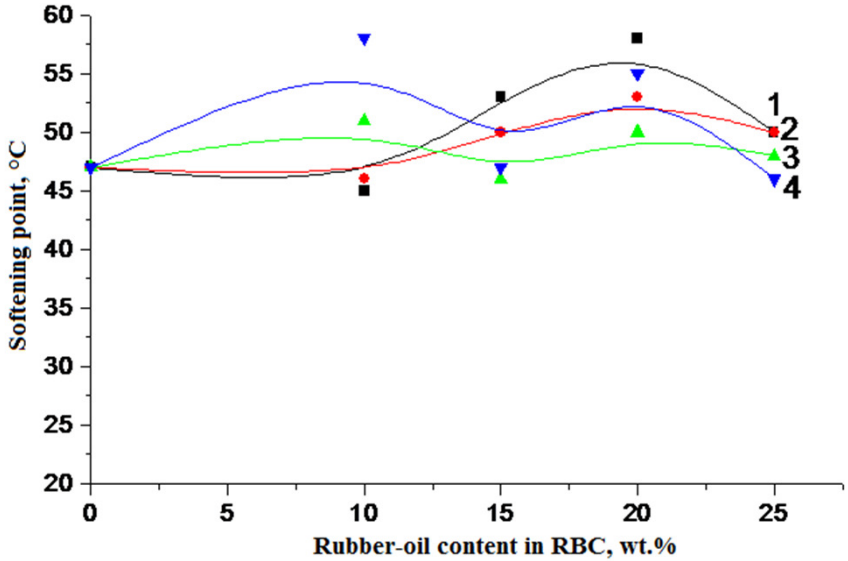
Physical and mechanical characteristics of RBC with rubber crumb (0.6-1 mm)

Names of indicators	Rubber-oil ratio	Rubber-oil percentage in bitumen				Method of testing
		10 wt%	15 wt%	20 wt%	25 wt%	
Penetration at 25 °C, 0.1mm	R:O=1:1	67	71	90	91	According to standard 11501
	R:O=3:2	87	160	195	108	
Softening point, °C	R:O=1:1	50	59	51	58	According to standard 11506
	R:O=3:2	53	45	45	52	
Ductilityat cm	R:O=1:1	12	13.5	12.5	11.5	According to standard 11505
	R:O=3:2	17	20	18	13	
Penetration index	R:O=1:1	-0.5	1.8	0.6	2.3	By empirical formula
	R:O=3:2	1.0	0.9	1.8	1.5	
Changing of softening temperature after heated, °C	R:O=1:1	4	4	5	5	According to standard 18180
	R:O=3:2	4	6	6	5	
Standard accordance	R:O=1:1	–	RBC 60/90	–	–	According to R RK 218-76-2008
	R:O=3:2	RBC 60/90	RBC 130/200	RBC 130/200	–	

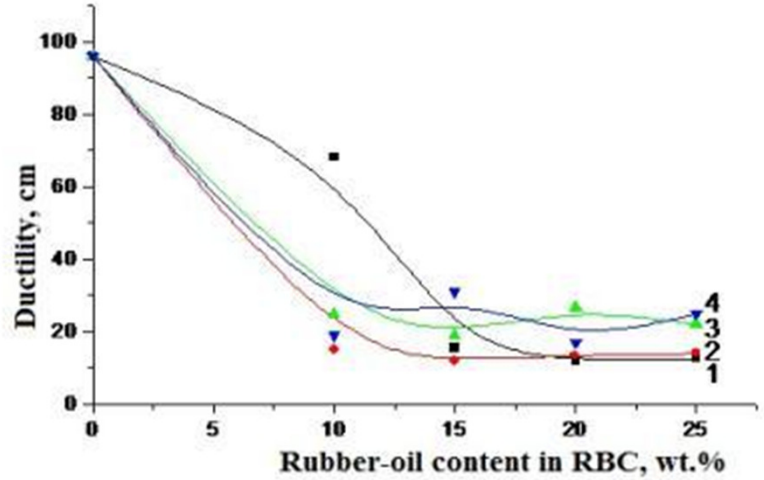
PROPERTIES COMPARISON OF ACTIVATED CRUMB RUBBER MODIFIED BITUMENS



Dependence of penetration on the rubber-oil content of RBC
Rubber-oil ratio: 1 – 1:2, 2 – 2:3, 3 – 1:1, 4 – 3:2



Dependence of softening point on the rubber-oil content of RBC
Rubber-oil ratio: 1 – 1:2, 2 – 2:3, 3 – 1:1, 4 – 3:2

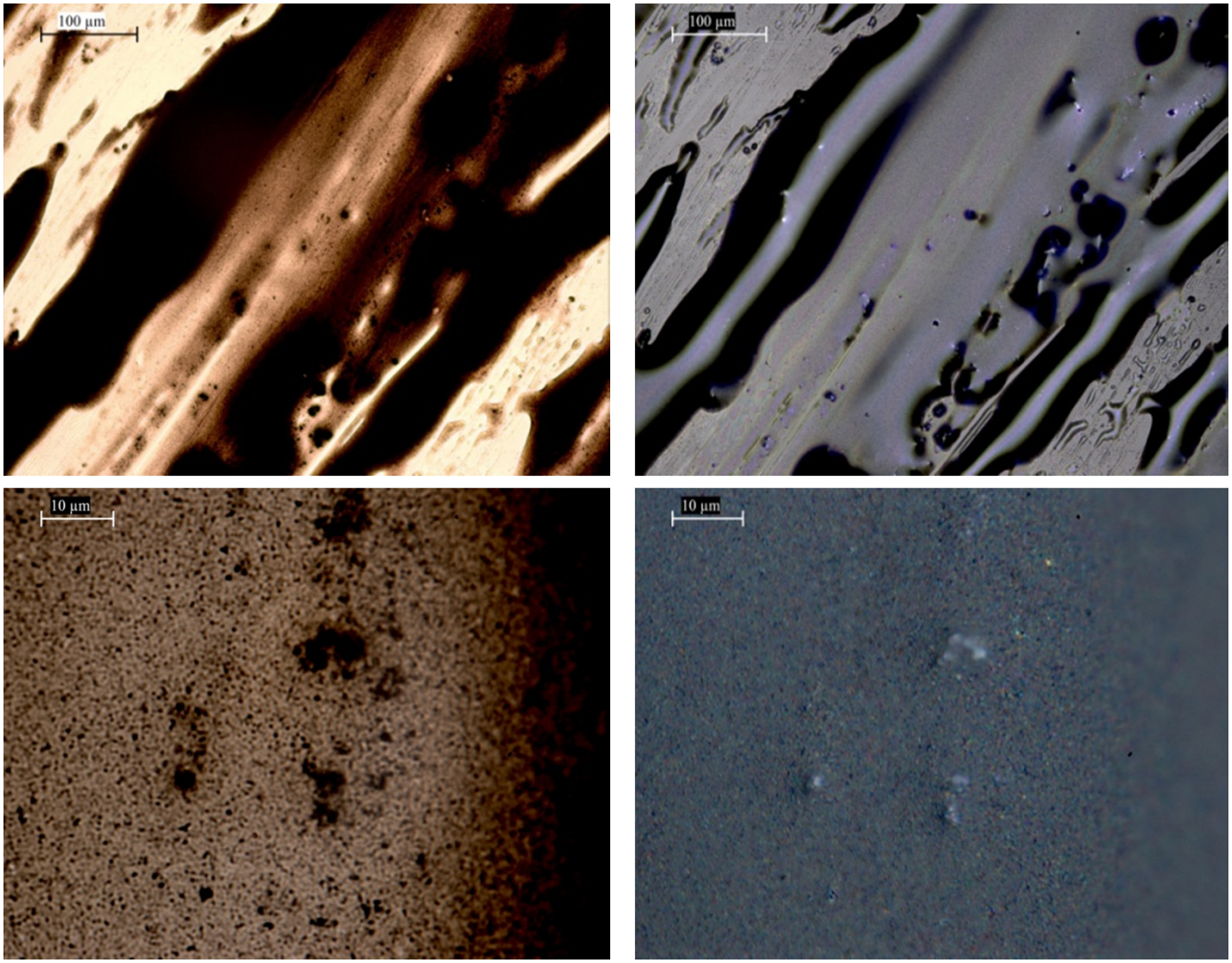


Dependence of ductility on the rubber-oil content of RBC

Properties comparison of crumb rubber modified bitumen with base bitumen

Kind of modifier	Penetration, 0.1mm	Softening point, ºC	Ductility, cm
Base bitumen	78	47	96
Rubber crumb, 10 wt.%	52	57	7
Rubber-oil mixture, 20 wt.%	126	50	26,5

MICROSCOPIC STUDY OF RUBBER -BITUMEN COMPOUNDS



Optical microscopic image of RBC

Physical and mechanical characteristics of rubber-asphalt with rubber crumb (less than 0.6 mm)

Name of indicators	Asphalt mix with rubber crumb				Standard requirements
	№ 1 RBC R:O=5:6 20 wt.%	№ 2 RBC R:O=1:1 20 wt.%	№ 3 RBC R:O=3:2 10 wt.%	№ 4 RBC R:O=3:2 20 wt.%	
Medium density, g/cm^3	2.34	2.33	2.35	2.33	Not rated
Water saturation, %	0.7	0.5	0.4	0.7	For the dense type from 1,5 to 4,0
Compression strength, MPa, at 20 °C water-saturated	2.4	2.0	3.1	2.1	Not rated
Compression strength, MPa, at 50 °C	0.7	0.8	0.9	1.1	For the dense type, MPa, not less than: A – 1.5 B – 1.8
Compression strength, MPa, at 0 °C	5.7	2.3	7.6	6.9	No more than 13.0 for the A, B type of asphalt concrete
Water resistance	0.89	0.83	0.97	0.89	Not less than 0.9
water resistant with prolonged water saturation	0.85	0.92	0.94	0.90	Not less than 0.8

Physical and mechanical characteristics of rubber-asphalt with no rubber crumb (0.6-1.0 mm)

Name of indicators	Asphalt mix with rubber crumb			Standard requirements
	№ 1 RBC R:O=5:6 25 wt.%	№ 2 RBC R:O=1:1 15 wt.%	№ 3 RBC R:O=3:2 20 wt.%	
Medium density, g/cm^3	2.30	2.31	2.28	Not rated
Water saturation, %	1.3	2.4	3.0	For the dense type from 1.5 to 4.0
Compression strength, MPa, at 20 °C water-saturated	1.5	2.3	2.1	Not rated
Compression strength, MPa, at 50 °C	0.6	0.8	0.8	For the dense type, MPa, not less than: A – 1.5 B – 1.8
Compression strength, MPa, at 0 °C	3.6	6.8	6.7	No more than 13.0 for the A, B type of asphalt concrete
Water resistance	0.88	0.96	0.78	Not less than 0.9
water resistant with prolonged water saturation	1.0	1.2	0.93	Not less than 0.8

GAS COMPOSITION, WHEN PREPARATION OF RBC AND AC BASED ON RC

The concentrations of gasesallocated in the preparation of rubber-bitumen compounds

Gases	Bitumen BND 60/90	Bitumen with rubber crumb of 7 wt.%	Bitumen with rubber-oil mixture of 20 %, 1:1
	Gas concentration, ml		
Methane	$1.4 \cdot 10^{-6}$	$3.2 \cdot 10^{-6}$	$13.3 \cdot 10^{-6}$
Ethan	$0.4 \cdot 10^{-6}$	$0.6 \cdot 10^{-6}$	$2.6 \cdot 10^{-6}$
Ethylene	$0.2 \cdot 10^{-6}$	$0.7 \cdot 10^{-6}$	$1.3 \cdot 10^{-6}$
Propane	$0.7 \cdot 10^{-6}$	$0.6 \cdot 10^{-6}$	$2.1 \cdot 10^{-6}$
Propylene	$0.4 \cdot 10^{-6}$	$0.4 \cdot 10^{-6}$	$4.1 \cdot 10^{-6}$
Isobutane	$0.1 \cdot 10^{-6}$	$0.1 \cdot 10^{-6}$	$0.3 \cdot 10^{-6}$
N-butane	$0.3 \cdot 10^{-6}$	$0.3 \cdot 10^{-6}$	$0.7 \cdot 10^{-6}$

The concentrations of gases, allocated in the preparation of asphalt mixtures

Gases	Stirring crushed stone, sand and mineral powder	Stirring crushed stone, sand and mineral powder with RBC
	Gas concentration, ml	
Methane	$2.1 \cdot 10^{-6}$	-
Ethan	$0.5 \cdot 10^{-6}$	$1.8 \cdot 10^{-6}$
Ethylene	$2.8 \cdot 10^{-6}$	$0.9 \cdot 10^{-6}$
Propane	$1.0 \cdot 10^{-6}$	$1.1 \cdot 10^{-6}$
Propylene	$14.2 \cdot 10^{-6}$	$10.0 \cdot 10^{-6}$
Isobutane	$0.1 \cdot 10^{-6}$	$0.2 \cdot 10^{-6}$
N-butane	$0.3 \cdot 10^{-6}$	$0.5 \cdot 10^{-6}$



Asphalt pavement with rubber crumb on the experimental plot of the Institute of Combustion Problems

CONCLUSION

1. Organic part of oil sand was carried out by extraction methods. Physicochemical properties of natural bitumen from oil sand was studied.
2. Extracted natural bitumen oxidized and produced bitumen at lower temperature and short time. The optimum content of the oil sands in the asphalt concrete were concluded at 28 and 47 mass %.
3. Synthetic oil were produced from oil sand by thermal processing of oil sand and Catalytic hydrogenation of natural bitumen. At the process active coal supported nanocatalyst were used.
4. It was precipitated asphaltene from natural bitumen of oil sand. Microscopic images showed that the asphaltenes have a medium-ordered structure, the main component of the surface is represented by amorphous carbon and asphaltene particle size around 40-50 nm. After heating asphalteneat high temperature and under inert gas 5.12 nm sized carbon composition materials were formed.
5. It is established that the optimal composition of rubber-oil at a ratio of 1:1 and 3:2 and introduction them to bitumen in optimal amount of 15-25 wt.%. It was prepared asphalt mixtures based on rubber-binders, which are physical and mechanical properties comply with the requirements of the standard.
6. Microscopic analyses of bitumen materials were concluded as following:during the preparation of rubber and bitumen, the bitumen aggregation almost covered the swelled rubber crumb when heating and stirring the mixture. It is important for react rubber crumb with bitumen; Sand grains of oil sand surrounded by natural bitumen and very thin layer of wetted water, keeping it separate each other. This phenomenon is more useful at processing and developing of oil sand.

Thank you for your attention!!!