New Technology for Efficient and Environment Friendly Treatment of Various Secondary Energy Resources

Olexandr YEGURNOV[1)]*, Sergiy BORUK*[2)]*, Igor WINKLER*[2)]*,*
Aleksey STROMENKO[3)]*, Natalya TROYANOVSKA*[2)]

[1)] "ANA-TEMS" corporation, Yuzhnyi St., 4 "b", Dnipropetrovsk, 49044, Ukraine; email: yegurnov@yahoo.com
[2)] Yu. Fedkovych National University of Chernivtsi, 2 Kotsybynsky St., Chernivtsi, 58012, Ukraine; email: s_boruk@hotmail.com, i.winkler@chnu.edu.ua
[3)] National Academy of Metallurgy, Haharina Ave, 4, Dnepropetrovsk, Dnipropetrovsk Oblast, 49600 Ukraine; tel.: +380 562 474 433, email: nmetau@nmetau.edu.ua, canc@metal.nmetau.edu.ua

Abstract

It is shown that liquefaction of the oil slurry by liquid polymer pyrolysis products ensures its utilization as secondary fuel. Low-caloric solid energy carriers can be used for additional stabilization of this fuel. This solution facilitates gradual substitution of some expensive and insufficiently available in Ukraine traditional energy carriers such as black oil, diesel fuel and others.

Keywords: oil slurry, coal concentration wastes, liquid polymer pyrolysis products, sedimentation stability, viscosity

Introduction

Rapid and efficient solutions related to switch to the own available and inexpensive resources are requested by the current difficult situation in the energetics of Ukraine. Ukraine possesses significant deposits of the low-caloric coal that can be involved into regular use and widen the national energetics base. Besides, it can also involve various waste and non-conditional materials formed in course of coal concentrating. Solid coal waste materials contain various toxic pollutants and are inclined to self-combustion which is very difficult to extinguish. The raw base of firm fuel with low calories content always gets wider in case of coal's software's wastes in the form of sludge. It is known that such materials can be used as the secondary fuel and burnt directly. However, such process releases significant amount of environment pollution agents while its technological efficiency is also quite low.

It's also accumulates many other wastes with fuel content. Oil processing technologies releases various semi-liquid oil slurries, which are being collected in the oil-sludge ditches. This technology cannot provide isolation of the soils and soil waters from constant leakage of the toxic oil components resulting in worsening in the environment safety of the oil-refining plants neighborhood. This situation is especially unfavorable in the regions with high level of the soil water.

The content of the volatile compounds in the oil slurries is usually lowering with time complicating their utilization as the secondary fuel component. Such slurry consists of much water that results in rather high flash point temperature (over 300°C). Besides, the slurry is liquid but very viscous and can hardly be excavated.

Another environmental problem is related to accumulation of various plastic debris and wastes. Pyrolysis is one of the most efficient and environmentally safe ways of utilization of the plastic but it results in formation of some liquid byproducts. These byproducts can also be used as the secondary energy carrier but they cannot be burnt directly because of inappropriate composition (see Table 1) and too low flash point temperature (up to 75°C).

It seems prospective to develop the mixed and averaged secondary fluent from all the above mentioned components. This fuel should be suitable for direct burning in the heating boilers and consist of the coal suspensions, ground coal and oil slurries. The latter component should be previously liquefied by adding liquid residue byproducts of plastic pyrolysis (Urev, 1980, 1985; Makarov et al, 1989, 2007; Degtyarenko et al, 1990; Gamera et al, 1990, 1999; Boruk and Winkler, 2008; Boruk, 2011).

Materials and methods

Following mixtures have been investigated in the framework of our work:

– oil slurry from the oil & gas production company "Dolynanaftogas". This is viscous dark brown product with the following parameters: density 0.912–0.937 g/sm³, viscosity 16.3 Pa s; water content about 32%, mineral compounds content 11–15%;

Tab 1. Composition of the pyrolysis liquid fraction with distillation temperature 55–185°C

Tab. 1. Skład frakcji ciekłej pirolizy przy temperaturze destylacji 55–185°C

Component	Content in distillation products, %
Non-aromatic compounds	14,6
Benzene	15,1
Thiophene	0,4
Toluene	6,1
M+p-xylenes	13,8
O-xylene	4,7
Naphthalene	0,5
Non identified compounds	44,8

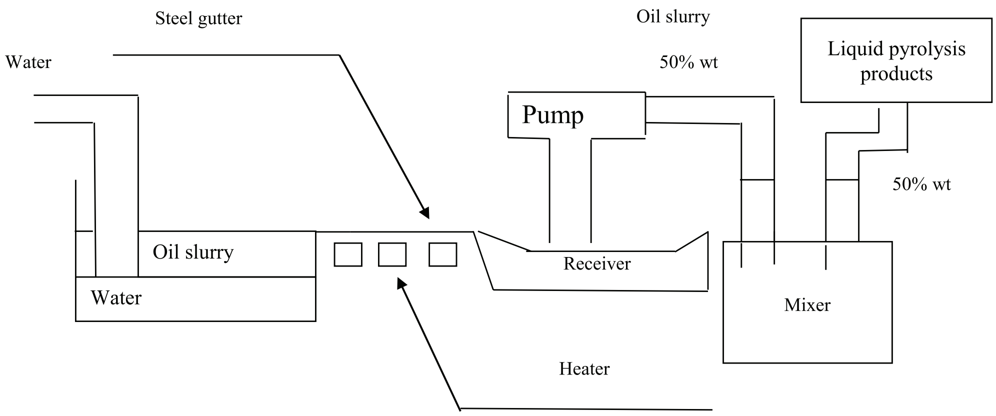

Fig. 1. Technological flowchart of the oil slurry excavation and liquefaction

Rys. 1. Schemat technologiczny upłynniania wydobytych szlamów olejowych

– oil residue from the crude oil storage vessels. Density 0.956–1.02 g/sm³; viscosity 12.6 Pa s; water content 24% and mineral compounds content 7–9%.

It should be mentioned that the accumulated amount of the oil residue is quite limited. It can reach up to 50–70 thousand tons for 5 years and they are being removed from the oil storage tanks in course of the regular service works. That is why, in our opinion, oil slurry is more promising source material. Rough estimation of the slurry amount collected in our region gives about hundred thousand tons and it is still growing. They are stored in the open slurry ponds and tanks and gradually lose volatile compounds thereof. As a result, the flash point temperature of the slurry is usually above 300°C, which makes their direct utilization as a fuel impossible unless the stage of preliminary heating is included in the scheme.

Results and discussion

We propose the multistage technological flowchart of processing and treatment of these secondary fuel components. First stage assumes excavation and liquefaction of the oil slurry (see Fig. 1)

The steel gutter should be installed at the edge of the oil slurry ditch. The gutter should be tilted towards the steel receiving tank (volume ca. 10 m3). As mentioned above, long storage of the oil slurry results in its layering into the bottom water/oil products and the surface oil products/water layers. Water content of the latter may be up to 30%. The slurry should be extruded out of the pond by pumping water in its bottom part. As a result, the slurry level will raise and some portions of the mixture start to outflow through the gutter. It should be heated up to 350 ÷ 380 K in order to make the slurry less viscous and let it run into the receiver. Then it should be pumped to the mixer and stirred with the liquid plastic pyrolysis products. Components weight ratio 1:1 ensures viscosity of the final mixture less than 1 Pa·s. Therefore, further transportation of such low viscous liquid can be performed by regular pumps. The residual water in the pond must be either treated or utilized in the water/coal suspension production and the empty pond can be drained out, filled with soil and reclaimed. An alternative procedure assumes further exploitation of the emptied ponds to store dewatered drilling fluids.

Tab. 2. Some technical parameters of the systems "oil waste – liquid pyrolysis products (LPP)"

Tab.2. Zestawienie niektórych parametrów technicznych systemu "odpady olejowe- ciekłe produkty pirolizy (LPP)"

№	Composit.: oil residue + LPP	Viscosity, Pa·s			Clarified layer height, mm			Calorific value, kJ/kg	Flash point temperature, K
		1 h	24 h	72 h	1 h	24 h	72 h		
Oil residue									
1	LPP	0,2	0,2	0,2	–	–	–	48800	350
2	Oil residue	–	–	–	–	–	–	28500	450
3	4 : 1	1,80	1,89	2,24	–	–	1	34350	410
4	3 : 1	1,30	1,45	1,75	1	2	4	36500	400
5	2,5 : 1	1,20	1,34	1,60	2	3	5	38600	390
6	2 : 1	1,10	1,25	1,50	3	6	8	52800	380
7	2,5 : 1 + 10% coal	1,50	1,60	1,74	1	2	2	43150	410
8	2,5 : 1 + 10% pyrocarbon	1,55	1,73	1,84	1	1	2	35400	410
Oil slurry									
1	Oil slurry	–	–	–	–	–	–	27200	600
2	8,5 : 1,5	1,54	1,64	1,75	–	–	1	32500	470
3	4 : 1	1,46	1,62	1,70	–	1	2	34100	450
4	3 : 1	1,23	1,34	1,40	–	1	3	36250	440
5	7 : 3	1,11	1,21	1,36	1	3	4	38000	410
6	6,5 : 3,5	1,03	1,15	1,21	2	4	7	39450	400

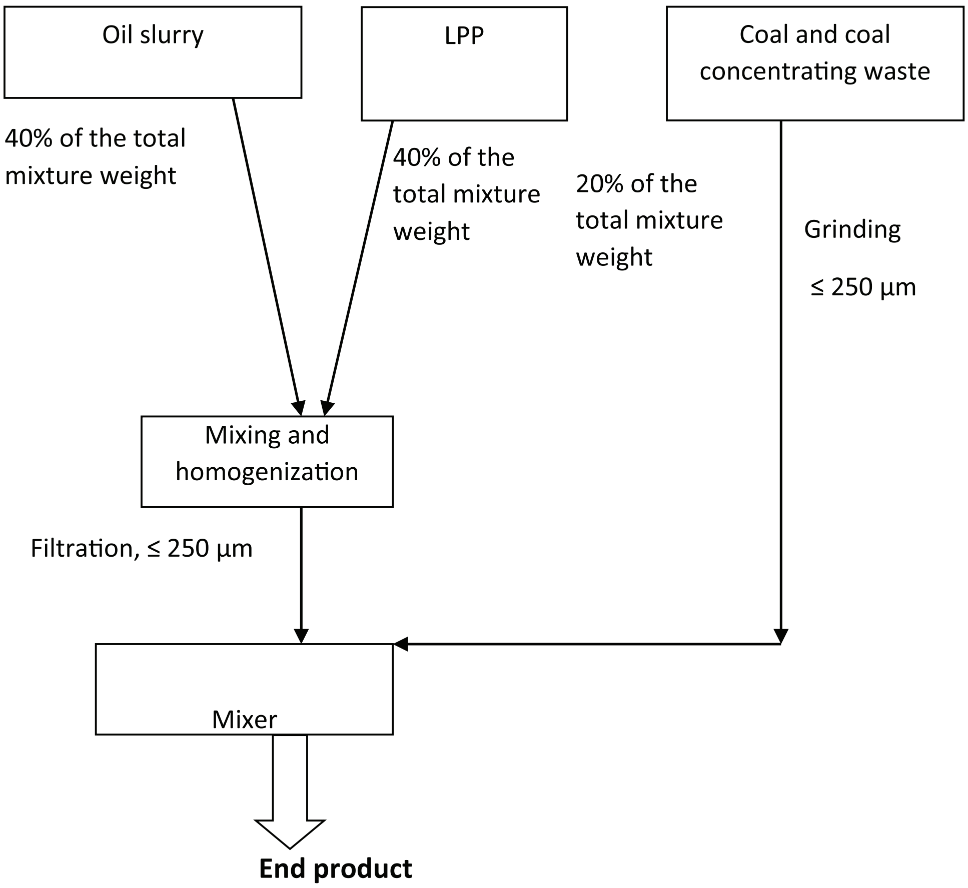

Fig. 2. Manufacturing scheme for the suspended coal fuel containing various secondary energy carriers

Rys. 2. Schemat produkcji płynnego paliwa węglowego zawierającego różne wtórne nośniki energii

Tab. 3. Physico-chemical, exploitation and environmental parameters of the composite fuel based on the secondary fuel sources

Tab. 3. Parametry fizyko-chemiczne, eksploatacyjne i środowiskowe paliwa kompozytowego wytworzonego z wykorzystaniem wtórnych nośników energii

Sample	Effective viscosity, Pa×s	Sedimentation stability, days	Burnout degree (%)	Calorific value (kJ/kg)	Specific emission of SO_2, kg/GJ
Source mixture (LPP + oil slurry)	0,45	8	100	38600	0,680
Source mixture + 20% «G» brand coal	0,86	19	99,5	43250	0,720
Source mixture + 20% waste of «T» brand coal	1,05	23	98,0	41500	0,560
Source mixture + 20 % brown coal	0,95	22	98,5	42000	0,640
Source mixture + 20% anthracite	0,75	14	99,3	41200	0,660
Source mixture + 20% pyrocarbon	1,25	28	96,5	44500	0,700

It was found that the mixtures obtained by the above procedure can be used as a fuel (see Table 2). As seen from Table 2, the best performance parameters (calorific value, flash point temperature) were determined for the mixtures based on the liquid plastic pyrolysis products and the oil residue. It is clear that the mixture's viscosity decreases with increase in the pyrolysis products weight fraction. The oil residue-containing systems exhibit higher viscosity and better sedimentation stability than the oil slurry based mixtures. Direct burning of this fuel is possible because its flash point temperature is comparatively low. This conclusion has been verified using the modified burner installed in the standard solid fuel boiler E-09/01 with full steam productivity 1000 kg/h. Special attention should be given to the performance indexes of the mixtures of oil residue and pyrolysis products with the components weight ratio 2:1 because the most effective ratio between the organic substances, water and mineral compounds, and the highest catalytic activity of the latter are ensured at such composition. In other words, the highest burnout degree can be achieved in such mixtures due to highly effective microheterogeneous catalysis on the mineral substrate supported by partial decomposition of water improving total calorific output of the fuel.

Physico-chemical properties of the oil residue and oil slurry based compositions are quite close while their exploitation characteristics are rather different. The slurry-based compositions with the components weight ration 1:1 are suitable for the direct burning but their sedimentation stability is low and they can get separated into the heavy and light fractions. On the other hand, some admixtures of the dispersed coal result in higher stability and better calorific productivity of such systems.

The suspended coal fuel preparation has been carried out according the following scheme (Fig. 2).

The dispersed coal materials of various parameters have been used to stabilize the fuel mixtures. Physico-chemical parameters of the fuel systems are represented in Table 3. They were partially determined in the laboratory research and during testing of the pilot burning equipment (Table 4).

A preliminary estimation of the expected economy effect of implementation of this technology at the firm "Bricket" is about 1 mln Ukrainian hryvnya annually.

Conclusion

Therefore, the following advantages of the proposed fuel can be outlined:

Environmental:

- better utilization of the dangerous wastes formed by the fuel compounds mining and refining, and some secondary fuel resources;
- high environmental and technical safety at all production, transportation and usage stages;
- reduction in pollutants emission to atmosphere, discharge to water objects and ground burial.

Technical:

- oilwater, oilwatercoal and watercoal suspensions are similar with the liquid fuel

Tab. 4. Environmental parameters of burning of standard fuel and secondary fuel mixtures

Tab. 4. Parametry środowiskowe produktów spalania standardowego paliwa i mieszaniny paliw wtórnych

Sample	Pollutants emission, mg/m^3	Air-gas emission temperature, °C
«G» brand coal	NO_2 – 12,60 CO – 850,0 SO_2 – 22,40	465
Fuel black oil	NO_2 – 7,86 CO – 545,3 SO_2 – 0,00	318
Suspension based on «G» brand coal	NO_2 – 12,81 CO – 193,9 SO_2 – 5,33	536
Suspension based on «G» brand coal + $Ca(OH)_2$	NO_2 – 9,05 CO – 175,2 SO_2 – 0,00	523
Suspension based on «T» brand coal	NO_2 – 16,23 CO – 492,9 SO_2 – 6,33	424
Suspension based on brown coal	NO_2 – 8,37 CO – 112,1 SO_2 – 0,00	376
Suspension based on anthracite	NO_2 – 2,05 CO – 606,3 SO_2 – 3,00	486
Suspension based on pyrocarbon	NO_2 – 18,11 CO – 691,46 SO_2 – 5,67	498

and can easily be applied to the existing equipment and technologies of the thermal energy production;

- the suspended fuel intake, transportation and boiler feeding stages can easily be turned automatic and mechanized;
- newly designed technology of the vortex burning ensures the flame temperature 950 ÷ 1050°C and burnout degree up to 97%.

Economic:

- 15 ÷ 30% decrease in the direct operating cost of the fuel storage, transportation and burning;
- the capital expenditure related to the boiler equipment conversion from natural gas or black oil to the suspended secondary fuel is 3 times lower than that for conversion to regular coal;
- the cost payback term for conversion to the secondary suspended fuel is about 1,0 ÷ 2,5 years.

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Nowa technologia efektywnego i przyjaznego dla środowiska przetwarzania różnych wtórnych zasobów energetycznych

W artykule zaprezentowano technologię upłynniania szlamów olejowych przy wykorzystaniu ciekłych produktów pirolizy polimerów, zapewniając ich wykorzystanie jako wtórnego paliwa. Zaprezentowana technologia umożliwia również zastosowanie niskokalorycznych stałych nośników energii do dodatkowej stabilizacji tego paliwa. Zastosowanie opracowanej technologii umożliwi stopniowe zastąpienie niektórych drogich i niewystarczająco dostępnych na Ukrainie tradycyjnych nośników energii, takich jak: mazut, olej napędowy i innych.

Słowa kluczowe: szlamy olejowe, odpady zawierające węgiel, ciekłe produkty pirolizy polimerów stabilność sedymentacji, lepkość