



Synergy in co-liquefaction of oil shale and willow in supercritical water



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HIGHLIGHTS

- A synergy occurs in the yields of oil shale and willow co-liquefaction products.
- The synergies are proportional with product of the shares of the components ($x_A x_B$) in the blends.
- The coefficient of proportionality, synergy factor, is the highest for the benzene soluble products.
- The synergy in the yield of benzene solubles is caused mainly by an increase in the yield of high polar heterocompounds.

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ABSTRACT

Co-liquefaction of oil shale kukersite and willow *Salix viminalis* blends by hydrous pyrolysis in supercritical water was studied under the conditions of 380 °C, 4 h, 38 MPa, and water/blend ratio 3/1 g/g. The actual yields of the consecutive products of extraction with various solvents did not agree with the additive values calculated by proportional contributions of the blend components. At any share of the components (x_A, x_B), the synergy (Δ) in the yields of the pyrolysis products estimated was proportional with the product of the shares of the components in the blend according to the equimolecular synergy model, $\Delta = \delta x_A x_B$. The values of the synergy factors, δ , decreased in the row of the products as follows $[(g/g)^{-2}]$: the oil soluble in benzene 62, acetone 11, water 9, and diethyl ether 5.6, solid residue –9.6 and the sum of gas and pyrogenetic water –79. The main increase in the yield of benzene solubles was result of the positive synergy in the yield of high polar heterocompounds, revealing the synergy factor $69\%(g/g)^{-2}$.

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1. Introduction

As reserves of conventional crude oil continue to decline, unconventional feedstocks have to be investigated and upgraded to meet the increasing demand for transportation fuels. The co-utilization of fossil fuels and renewable lignocellulosic biomass in production of liquid fuels would expand the feedstock resources and decrease the global CO₂ emission because of photosynthesis of growing plants. Besides, a synergy has been found in the yield and composition of the co-pyrolysis products by a number of researchers. Examples of interactions found in co-pyrolysis of fossil fuels, mostly coals, with biomass (BM) varieties and plastic (PL) wastes under various conditions and blend composition are presented in Table 1.

Table 1 shows that the weight loss for the blends of a coal with a BM variety is additive in the most of thermogravimetric (TGA) pyrolysis experiments [1–11]. Lack of synergy is explained by different temperature ranges of the thermal decomposition. Using, as

a rule, less than 20–40 mg of the blend samples, the position of dG/dT peak of any BM is about a hundred degrees lower than that of coal. So, the volatiles of BM origin leave the pyrolysis zone before thermal decomposition of coal starts. Nevertheless, it was found in [8] that above 800 °C the char yield in TGA increased for the blend consisting 10% of hazelnuts with peat but decreased with coal, anthracite and lignite. The TGA represented by Sonobe et al. [11] showed no synergy in the weight loss but revealed an exothermic secondary decomposition of the blends of Thai lignite and corncob. The oil yield had a positive synergy for the blend of PE with an oxygen rich coal and a negative one with oxygen low coal in the work of Yang et al. [12]. The TGA of Moroccan oil shale with PL mixtures [13,14] demonstrated increase in the thermal stability. Park et al. [15] established in TGA of the blend of coal and sawdust a positive synergy in weight loss above 400 °C.

According to Sharypov et al. [16] a synergy in the liquid yield in autoclaves can be explained by hydrogen transfer from a polyolefinic chain to BM radicals.

Lack of synergy in the yield and composition of co-pyrolysis products was found in drop tubes at high heating rates [4–7,17] but also at low heating rates in horizontal tubes [4–6].

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Table 1
Synergistic effects in co-pyrolysis.

Reference	Blend components	Device and conditions	Synergy
[1]	Coal + wood, animal and agricultural wastes	TGA, 200–800 °C, FTIR	No
[2]	Coal + wood waste, wheat straw	TGA, up to 1250 °C	No
[3]	Three different rank coals + pinewood, cellulose, lignin, xylan or polywax	TGA, Pyrolysis-GC-MS, 100 g, batch reactor, 520 °C	No. The shares of aliphatic and aromatic hydrocarbons are depressed
[4]	Coal + Radiata pine sawdust	200–1400 °C, horizontal tubes, high heating rate in a drop tube, 900–1400 °C, GC	No in the yields and gas composition
[5]	Coal + Radiata pine sawdust	Low heating rate in horizontal tube 200–1000 °C, high heating rate in a drop tube 900–1400 °C	No
[6]	Coal + Radiata pine sawdust	Low heating rate in a horizontal tube, 10–50 °C/min, high heating rate in a drop tube 10 ⁴ °C/s	No
[7]	Coal + swithgrass	Drop reactor, 900 °C, Pyrolysis GC-MS	No
[8]	Different rank coals + 10% hazelnut shells	TGA, up to 900 °C	Above 500 °C the char yield changed for the blends with (by%): peat- + 6.3, bituminous coal -2.7, anthracite -3.1, Soma lignite -5.5, Askale lignite -10.1
[9]	Brown coal + polyolefinic polymers	TGA, 300–1100 °C Autoclave, catalysts hematite and pyrrhotite	No. Conversion degree increased by 10–15% for the 1/1 blend
[10]	Beech, pine, cellulose or hydrolytic lignin + polyethylene (PE) or polypropylene (PP)	TGA, Autoclave, 400 °C	No for the blends BM > 50% but for BM < 50%, the liquid yield increased, and gaseous products and char yields decreased
[11]	Thai lignite + corncob	TG-MS, 300–600 °C Fixed bed reactor	No in the weight loss, but exothermic secondary decomposition of corncob is revealed. The char yield decrease by 9%, the yields of volatiles increased
[12]	Chinese coals + PE	TGA, 300–900 K	Oxygen rich coal (12% O) – negative synergy with HDPE and LDPE (max 8%). Oxygen poor coal (2% O) – positive synergy with HDPE (max. by 3%). The apparent activation energy of the blends is higher than waited
[13,14]	Moroccan oil shale + PL, 1/1.	TGA, 300–900 °C Autoclave, 500–525 °C	Thermal stability increased. Positive synergy for the blends with HDPE by 4.0%, LDPE by 4.7%
[15]	Coal + sawdust	TGA, Fixed bed reactor	Increase in weight loss above 400 °C. By 6% more gas and 3% less char was obtained for the 3/2 blend
[16]	Beech, pine, cellulose or hydrolytic lignin + PE or PP	Autoclave, 400 °C, FTIR, ¹ HNMR, GC-MS, TLC	Hydrogen transfer from a polyolefinic chain to BM derived radicals result in the higher yield of liquids
[17]	Dayan lignite + legume straw	Fast pyrolysis in a free fall reactor, 500–700 °C	At 600 °C and 73% of straw the char yield decreased and liquids yield increased by 10%
[18]	Coal + sawdust or olive stones, 25, 33, 50%	Fixed bed reactor, 600 °C	Released sulfur increased 1.81–1.33 times
[19]	Coal + rice straw, 1/4, 1/1, 4/1	High frequency furnace, 600–1200 °C	When coal prevailed in the blend, the yield of char decreased and of volatiles increased whereas oil yield increased at lower and gas yield at higher temperature region
[20]	Samca coal + C ₅₀ -alkane	Pyroprobe 1000 CDS, 900 °C	For all the blends, a positive synergy in the yields of CO, C ₂ H ₆ , C ₂ H ₄ , C ₄ H ₆ , and negative of C ₃ H ₈ and C ₄ H ₈ for the blends with 40% of coal and of aromatic hydrocarbons for the blend with 50% of coal
[21,22]	Estonian kukersite oil shale + LDPE. Dictyonema argillite + LDPE or kukersite	Autoclave, 420–540 °C, 20–120 min	No synergy in the yields of gas, liquids and coke The carbon number of aliphatic hydrocarbons decreased 1.5 times
[23]	Kukersite + pine wood in supercritical water	Autoclave, water/blend 3/1 g/g, 380 °C, 40 MPa, 4 h	Up to 1.5–1.9 times higher oil yield and lower yields of gas and solid residue due to formation of additional high polar heterocompounds
[24]	Pine wood + PE or PP	Autoclave, H ₂ 3 MPa, 400 °C, 5% iron ore catalyst	By 10–15% higher conversion degree, by 14–21% more liquids, the content of olefins and cycloparaffins sharply decreased
[25]	Coal + BM	TGA, 100–1000 °C, kinetics	No synergy in the weight loss. Co-pyrolysis kinetics is described by parallel-series reaction scheme with three regions with different activation energies
[26]	BM + PL	TGA, 100–650 °C, kinetics	By 6–12% increase in the weight loss. Co-pyrolysis kinetics was described by three consecutive reactions with activation energies 107–128 (BM), 164–249 (BM + PL) and 426–498 (PL) kJ/mol
[27]	Chinese low volatile coal + 5% of PL (LDPE, HDPE, PP)	TGA, kinetics, 100–650 °C	At 550–650 °C synergy in the weight loss by 2.0–2.7%. Three or four different reactions with activation energies between 35.7 and 573 kJ/mol and frequency factors between 27 and 1.7 × 10 ³⁸ min ⁻¹
[28]	Indian coal + LDPE 1/3, 1/1, 3/1	TGA, 36–900 °C, n-order kinetic model	No synergy when coal prevails. Increase in the weight loss by 8% for the 3/1 blend, the kinetic constants for blends do not vary significantly
[29]	South Korea sub-bituminous coal + RDF (47.9% of paper, 30.8% of PL, 10.3% of textile, and 9.2% of wood), for 9/1, 4/1, 1/1	TGA thermobalance reactor, kinetics	The decomposition degree of the blends is by 3.2–5.7% higher than the calculated values. In the isothermal condition, activation energies of coal and RDF blends are lower

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