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LOW-TEMPERATURE PYROLYSIS AND CO-PYROLYSIS OF GÖYNÜK OIL SHALE AND TEREBINTH BERRIES (TURKEY) IN AN AUTOCLAVE

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Low-temperature pyrolysis of Turkish Göynük oil shale (GOS) and terebinth berries as individual objects and their dry and hydrous co-pyrolysis in a closed system, in an autoclave was studied. The effect of pyrolysis conditions (temperature and duration) on the yield of extracts (hexane and benzene), gas and organic residue was investigated.

The composition of extracts was determined via thin layer chromatography. The yield of the extracts increased with the increase of pyrolysis temperature and duration, and its maximum attained 48.5% from the initial organic matter for GOS and 40% for berries. On the other hand, supercritical water also affected product yields and composition of extracts derived from both GOS and terebinth berries. The total yields of extracts from hydrous pyrolysis were 57.3% and 60.0% for GOS and berries, respectively. However, the extracts of hydrous pyrolysis contained more polar heterocompounds and less nonaromatic hydrocarbons than those of dry pyrolysis.

Addition of berries to GOS lowered the co-pyrolysis temperature about 10 °C for reaching the maximum yield of the total extract. Dry co-pyrolysis of GOS with berries resulted in additive rather than in synergistic effect in the total extract yield, but the composition of the extract as a fuel – more nonaromatic hydrocarbons (33.8%) and less heterocompounds (43.0%) than that of extracts from individual feedstocks – was improved. Similarly, in the case of hydrous co-pyrolysis, the yields of extracts (hexane and benzene), gas and organic residue consisted of partial contributions of the yields from the initial feedstocks.

Introduction

The world energy crises and large increases in the prices of oil derivatives have caused renewed interest in carbonaceous material, especially renewable

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ones, as an energy source. Synthetic gaseous or liquid fuels are obtained by converting a carbonaceous material to another form using thermo-chemical processes such as pyrolysis, gasification and liquefaction. The most abundant naturally occurring materials suitable for this purpose are coal, oil shale, biomass and organic wastes. Oil shales, which are kerogen-rich sediments, are promising resources for long-range alternatives to crude oil. For many countries oil shale represents a valuable potential source of liquid hydrocarbons and energy. The deposits of oil shale are widely distributed throughout the world. Kerogen, commonly defined as the insoluble macromolecular organic matter (OM) dispersed in sedimentary rocks, is by far the most abundant form of OM on Earth. Kerogen is a major sink in the global carbon cycle and represents by far the largest OM pool on Earth – 10^{16} tonnes of C compared to *ca.* 10^{12} tonnes in the living biomass [1]. Oil shales vary widely in geological age, genesis, chemical composition and organic matter content, and that is why there are substantial differences in their chemical decomposition regularities. Oil shale is processed through pyrolysis (retorting process) to yield shale oil in China, Estonia and Russia, as well as to generate the electric power by combustion.

Investigating pyrolytical behavior of Australian, Brazilian, American, Israeli, Swedish, Chinese, Moroccan, former Yugoslavian, Polish, Canadian and Turkish oil shales, it was demonstrated that their pyrolysis kinetics differ. However, a common feature noted in the kerogen liquefaction process of these oil shales is that shale oil does not form directly from kerogen but *via* bitumen as an intermediate. So, the pyrolysis of oil shale kerogen was described by a two-step mechanism involving two consequtive first-oder reactions, the first step being the degradation of kerogen to bitumen, and the second step being the decomposition of the bitumen to oil, gas and carbonaceous residue as final products [2–4]. The composition and solubility of thermobitumen depend on pyrolysis conditions and its ageing [4, 5].

Oil shales comprise the second largest solid fuel reserve in Turkey, after lignites, with reserves totaling approximately 2,220 million tonnes and located mainly in Göynük Himmetoğlu, Seyitömer, Beypazarı, and Hatıldag deposits [6–8]. There are many studies in literature relating to Turkish oil shales.

Kök et al. [9–11] have investigated the combustion kinetics of different kind of Turkish oil shales under non-isothermal conditions using TG/DTG and differential scanning calorimetry (DSC). The results showed that activation energy increases with OM content of oil shale samples and heating rate.

Pyrolysis kinetics of Göynük Himmetoğlu, Mengen and Can oil shales was studied also by using TG/DTG and DSC under nitrogen atmosphere [12]. Experiments showed that two different mechanisms led to mass loss: distillation between 22–227 °C, visbreaking and cracking in the region of 227–527 °C. The maximum product release temperature for Göynük oil shale (GOS) was found to be ~440 °C during the pyrolysis in a fixed-bed reactor [8].

Effect of demineralization on the yield and composition of volatile products from Turkish shales has been studied in many investigations [13–15]. At non-isothermal pyrolysis of the HF-washed GOS, the percentages of volatiles were about 20% higher than those at pyrolysis of the unwashed oil shale [13]. The results indicated that oil shale components washed out with HF, namely silicates, inhibited the pyrolysis reactions. Inhibition effect of silicates was greater than the catalytic effect of carbonates. The activation energy of pyrolysis reactions of silicate-free oil shale was lower than that of both original and carbonate-free oil shale. Similarly, at isothermal pyrolysis of the HF-washed GOS, volatile hydrocarbon recovery (VHR) increased nearly by 10 wt% as compared with VHR from unwashed oil shale [14, 15].

Recently, a number of processes, such as fluidized-bed pyrolysis and hydro-retorting, have been developed to obtain higher oil yields than attainable by the conventional retorting process. Liquefaction of oil shale using supercritical fluid extraction has also gained particular interest due to its striking advantages such as high destruction efficiency of OM attainable in a compact equipment and resulting in less charring [16–18]. Thermal dissolution of Estonian kukersite oil shale in the presence of supercritical water and some organic solvents was accelerated in comparison with low-temperature pyrolysis of kukersite without any solvent [18]. However, the liquid product was mainly unsaturated thermobitumen of high-molecular mass needing further upgrading to meet requirements for liquid fuel.

In literature, there are a number of studies with GOS such as slow and flash pyrolysis and hydropyrolysis [16]. Considerable differences were observed in the yields and compositions of the oils obtained under different conditions. The results showed [16] that supercritical (SC) water acted not only as a solvent but also reacted with organic matter in oil shale. It led to higher oil yield compared with slow and fast pyrolysis, but this oil contained a high proportion of asphaltenes and polar compounds.

Another approach in utilization of oil shale is co-processing. In literature, there have been some studies on co-processing of oil shale with plastics [19–22]. On the other hand, the oil shale/biomass co-processing is one of the most promising options for enhanced liquefaction of oil shale and preferable liquefaction products. Co-processing can also provide environmental benefits leading to reduction in CO_2 emissions. The previous study [23] showed that the pyrolysis characteristics of biomass are quite different from those of oil shale. The shale oil was almost totally soluble in benzene while the bio-oils obtained from wood, bark and needles, were mostly water-soluble.

Co-liquefaction of biomass and oil shale in SC water can be proposed with the intention that hydrogen transformation between biomass and oil shale takes place, resulting in enhanced liquefaction of oil shale and preferable liquefaction products. In literature, there is a number of studies on co-processing of biomass with coal [24], but less studies on co-processing of oil shale with biomass [25–27]. Co-liquefaction of kukersite oil shale and pine wood in SC water gave synergistic effect: the yields of solid residue and gas with pyrogenetic water were reduced by 1.7–2.0 and 1.4–2.0 times, while the yield of the most expected component of oil – benzene-soluble part – was 1.5–1.9 times higher than additive yields [27]. However, water-conversion oils from kukersite and wood mixture were richer in heterocompounds than the oils from single objects.

The biomass used in this study is terebinth berry – the fruit of terebinth (*Pistacia terebinthus*). In Turkey, terebinth is found growing in southern Turkey. The fruits are rich in protein, oil, fibre and unsaturated fatty acids [28]. Kumar and Gupta studied biocrude production from switchgrass using SC water [29]. Obtained results showed that the treatment with SC water caused a complete breakdown of lignocellulosic structure of switchgrass, and at that dehydration of biomass was favoured over hydrolysis reactions at the high temperature (260 °C). In another study relating to hydrolysis of cellulose in sub- and supercritical water, it was postulated that reactions below 240 °C led to the formation of water-soluble products, whereas reactions above 260 °C led to the formation of oil, char and gaseous products [30]. Similarly, at liquefaction of straw in the presence of hot compressed water [31], it was observed that during heating from 200 to 220 °C, the main reaction was the hydrolysis of cellulose and hemicellulose leading to the formation of water-soluble products. But, with the temperature continuously increased to 310 °C, the reaction of repolymerization was more drastic compared to hydrolysis; the water-soluble products were decomposed and repolymerized into gases and oily products.

The main objective of the present study was to investigate the effect of the biomass on thermal degradation of GOS in terms of both product distributions and liquid product properties. GOS, terebinth berries and their blend (1:1) were pyrolyzed at low temperatures in an autoclave. Some experiments were carried out in aqueous media. For the individual feedstock, the effect of pyrolysis conditions (temperature and reaction time) on the properties of the liquid product was investigated.

Although there has been a significant amount of work on pyrolysis/liquefaction of GOS, there is no study of co-pyrolysis of GOS with biomass. In this study, the goal was to find whether the addition of biomass to oil shale has positive effect enhancing oil shale liquefaction and favouring preferable liquefaction products.

Experimental

Materials

Oil shale samples from the Göynük Himmetoğlu deposit and terebinth berries were ground to the 120 μm particle size according to ASTM D2013 and used in experiments as received. GOS consists of more than 50% liptinite, 20–50% huminite, and 0–20% inertinite maceral groups and is characterized by high organic content. The origin of the organic matter is mainly algae and land plants, and the kerogen of GOS is classified as type I.

Some properties of GOS and terebinth berries are given in Tables 1 and 2, respectively.

Pyrolysis

Low-temperature pyrolysis experiments were performed with a sample of 4.0 g of powdered GOS, moisture 7.04%, or terebinth berries, moisture 7.12%, in a micro-autoclave (V = 20 mL). After loading, the autoclave was placed into a muffle oven at room temperature. Then the oven was heated up to reaction temperature (340–440 °C) for a heating period about 100 min. The autoclave was kept at the desired reaction temperature for different residence times varied from one to three hours. After the residence time used, the autoclave was cooled to room temperature, opened and gases were vented off. The mass of the gas formed was determined by the weight loss after discharging. The reactor content was extracted with *n*-hexane and benzene individually in a Soxhlet extractor according to ASTM D5369. The mass of the residue insoluble in benzene was dried at 105–110 °C. The percentage of OM in pyrolysis residue was estimated by subtracting of the mineral matter. After the removal of *n*-hexane and benzene in a rotary evaporator under reduced pressure, the fractions were weighed and designated as hexane and benzene extracts, respectively. In this study, the mass of extracts was also determined by subtracting the masses of gas and residue from the initial mass of dried shale after extraction with hexane and benzene, respectively. Product yields were calculated in wt% based on OM in the objects.

The mass of the extracts was found in two ways. The more used possibility to determine their mass is to evaporate the solvent from extracts till the constant weight (variant A). The other possibility (variant B) is calculation by the difference between the masses before and after extraction. In the case of hexane extract the hexane extraction residue is subtracted from the sum of pyrolysis products (without gas), benzene extract is calculated subtracting the benzene extraction residue from the hexane extraction residue. The details of the experimental process were provided in a previous study [5].

The analysis data of GOS and berries are given in Tables 1 and 2.

Table 1. **Characterization of Göynük oil shale**

Elemental composition of OM, wt%			Proximate analysis, wt% dry basis	
	[14]	[15]	Ash (A^d)	16.0
C	67.6	63.8	OM**	84.9
H	8.3	8.0	Sulphur distribution, wt% dry basis	
S	4.4		Total	3.76
N	1.3		Sulphatic	0.13
O*	18.4		Pyritic (S_p)	0.54
H/C	1.48	1.50	Organic*	3.09

*Calculated from difference.

**Calculated on acid-treated basis 100-A^d-0.625 S_p.

Table 2. **Characterization of terebinth berries**

Elemental composition of OM, wt%		Proximate analysis, wt%, dry basis	
C	49.5	Ash (A^d)	2.72
H	6.0	OM	97.28
S	0.2	Component analysis, wt%, dry basis	
N	3.2	Holocellulose	40.9
O*	41.1	Lignin	40.2
H/C	1.45	Extractives**	14.5

*Calculated from difference.

**Toluene/alcohol (2/1) (v/v).

Co-pyrolysis of GOS and berries

Co-pyrolysis experiments were made as dry pyrolysis without additional water and as hydrous pyrolysis with additional amount of water. In a typical run, 2 g of GOS and 2 g of berries (the OM ratio in the mixture was about 1:1) were mixed. Dry co-pyrolysis experiments were carried out in a 20 mL stainless steel batch autoclave at temperatures 340, 360, 380, 400, 420 °C and duration 2 h.

In the hydrous pyrolysis experiments of individual feedstocks the autoclave was charged with 2 g of GOS or berries and the required amount of water (4 mL for object:water ratio 1:2 and 6 mL for ratio 1:3). The autoclave placed into a muffle oven was heated to 380 °C (for GOS) or 340 °C (for berries) and was kept at this temperature for two hours. After the gaseous products were vented, the reactor contents were diluted with additional amounts of water and the water phase was poured from the autoclave onto the filter. The water-soluble compounds were extracted from the aqueous solution by diethyl ether and their mass was weighed after solvent evaporation. The rest pyrolysis products were extracted with *n*-hexane and benzene individually. The yields were determined as in the case of dry pyrolysis process. The hydrous pyrolysis of mixed GOS and berries was carried out in 100 mL autoclaves saving the filling ratio compared with 20 mL autoclaves.

Analysis of hexane extracts

Hexane extracts were separated into groups of compounds by preparative thin-layer chromatography (TLC) on 24-cm plates coated with 2-mm silica gel layer (60 mm, Fluka) and *n*-hexane as the eluent was used. TCL fractions represented nonaromatic hydrocarbons, monocyclic and polycyclic aromatic hydrocarbons, neutral and polar heterocompounds.

Result and discussion

Extraction of the initial feedstock

The initial GOS and berries were extracted with hexane and benzene at room temperature and the results are given in Table 3.

Table 3. **Yield of extracts from the initial GOS and berries, wt %/OM**

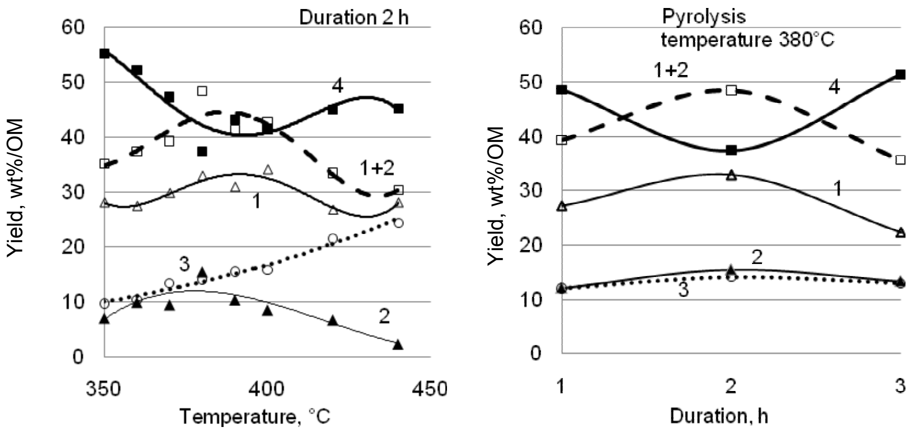
Extracts	GOS	Berries
Hexane	0.8	6.1
Benzene	6.5	2.5
Total	7.3	8.6

We can see a rather big quantity of hexane extract won from berries and benzene one from GOS.

Low temperature pyrolysis

In these group experiments, the effect of dry pyrolysis conditions, such as temperature and duration, on the yield of products was investigated.

To investigate the influence of temperature on the yield of products from shale, a series of experiments at varying temperatures (350 to 440 °C) were carried out at a pyrolysis time of 120 min. The results obtained are shown in Fig 1. In the case of oil shale, the gas yield gradually increased with increasing temperature, whereas total hexane and benzene extracts showed a maximum (about 48.5%) at 380 °C. As for thermal cracking reactions at high temperature, above 380 °C, repolymerization reactions led to an increase in the amount of organic residue. Comparing oil yields obtained in this study with oil yield from Fischer assay one can say that pyrolysis in a closed system produced larger amounts of extracts at lower temperature than conventional pyrolysis in an open system. However, if to compare the similar pyrolysis processes of the GOS and kukersite [5], it can be seen that GOS yields


(a)

(b)

Fig. 1. Göynük oil shale.
The effect of pyrolysis temperature (a) and pyrolysis duration (b) on the yield of hexane extract (curve *1*) and benzene extract (curve *2*), and total extracts (curve 1+2), gas (curve *3*) and organic residue (curve 4).

less extract than kukersite with maximum yields achieved at higher pyrolysis temperature. This is probably due to the catalytic effect of some inorganic compounds in kukersite.

In the case of berries, the total yield of extracts (hexane plus benzene extracts) reached a maximum (about 40.7%) at 340 °C that did not change up to 390 °C and was followed by further decrease (Fig. 2). The yield of organic residue did not change considerably with increasing temperature, while the gas yield increased continuously.

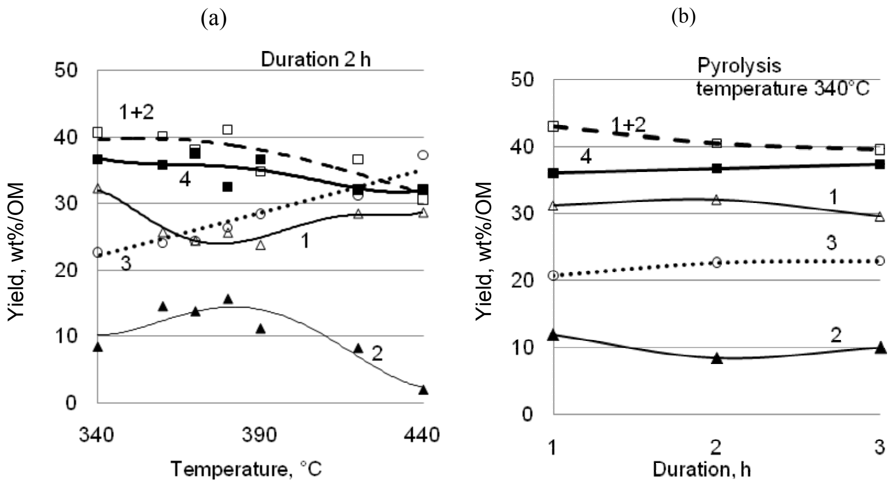


Fig. 2. Terebinth berries.
The effect of pyrolysis temperature (a) and pyrolysis duration (b) on the yield of hexane extract (curve 1) and benzene extract (curve 2), and total extracts (curve 1+2), gas (curve 3) and organic residue (curve 4).

For comparison purpose, a terebinth berries sample was also pyrolyzed at 400 °C in Fischer assay conditions. The details of the used pyrolysis system and separation of pyrolysis products can be found in a previous study [32]. Thus, 100 g of biomass were put into the reactor, the temperature was increased by a heating rate of 5 °C min^{-1} up to 400 °C and kept for one hour at the desired temperature. The total amount of liquid product was determined by difference. The yields of liquid products and char were determined by weighting. The amount of gas was determined by difference. The liquid product consisted of two phases; aqueous phase and oily phase. The aqueous phase was separated from the oily phase by funnel and weighed.

Pyrolysing the berries in the open system, we obtained the liquid products, which consisted of oily phase (21%) and aqueous phase (27%). The oily product contained water-soluble compounds (19.2 %), hexane extract (68.7 %) and benzene extract (12.1%). It is clear that pyrolysis of berries in the closed system yielded more extract than in the open system. It may be concluded that during thermal degradation an intensive intramolecular redistribution of oxygen took place, resulting in formation more tarry and gaseous products rather than water and water-soluble oxygenated compounds. It is noted that the extract yield obtained from berries is higher than that from other lignocellulosic material such as willow (22.8%) [27], sawdust (17.2%) [29], rice husk (8.6%) [34]. The reason for this is that both the yield and composition of the conversion products obtained in thermochemical conversion depend on operating conditions and on the chemical composition of the initial feedstock operated.

The effect of pyrolysis duration on the yield of products at temperatures for the maximum extracts yield, 380 °C for shale and 340 °C for berries is presented in Figures 1 and 2. For GOS (Fig. 1*b*), the yield of organic residue is minimum at the maximum of the yield of total extracts. This shows that at extended pyrolysis duration solubles are converted to organic residue by repolymerization. On the contrary, pyrolysis duration had no considerable effect on the yield of extracts for berries (Fig. 2*b*).

Pyrolysis temperature and duration had a significant effect on the yield and the composition of the obtained oil. The gas yield increases proportionally to the increase in temperature and duration. For GOS, the extract yield goes through a maximum at 380 °C (about 48.5% of total extracts). The duration affects more the yield of extracts, being less in short times, going also through a maximum and decreasing at longer duration. The same tendency was observed for kukersite – the increase in nominal temperature increases the yield of gas, decreases the yield of benzene extract, whereas the yield of hexane extract has its maximum at 400 °C and the yield of solid residue its minimum at 370 °C. The maximum yield of total hexane and benzene extracts was 80% from kukersite OM. So, the quantity of extracts from GOS (48.5%) is less than that from kukersite, and the maximum yields of extracts were obtained under different conditions. For berries, pyrolysis conditions do not affect the yield of extracts so noticeably. The yield of total extracts has the plateau within the temperature interval 340–380 °C and achieves 40% from OM.

As noticed before, the removal of solvent traces from extract has been a problematic procedure. The quantity of extracts can be underestimated due to evaporation of low-boiling destruction products or overestimated when a part of solvent, having higher boiling temperature or being connected with destruction products by H-bonds, is not entirely removed. Both variants (A and B) of estimation of extracts' yield for shale and berries are given in Figures 3 and 4, respectively. For oil shale, the quantity of benzene extract estimated by both variants is similar and does not depend on pyrolysis temperature. But the quantity of hexane extracts depends very strongly on the variant of estimation and pyrolysis temperature. For shale at higher pyrolysis temperature yielding more low-boiling destruction products, the difference between two variants of estimation is about 3.5 times, the weight losses of total extracts by variant A are about 60%. The same results were observed at storage of pyrolysed kukersite [5]. Independently of the pyrolysis temperature, during a month of ageing in the open air the weight loss reaches 10–15% from the initial weight of OM. On the contrary to berries, the quantity of benzene extracts estimated by both variants also depend very strongly from the variant of estimation and pyrolysis temperature. This shows that high pyrolysis temperature led to the formation of low-boiling products in benzene extract.

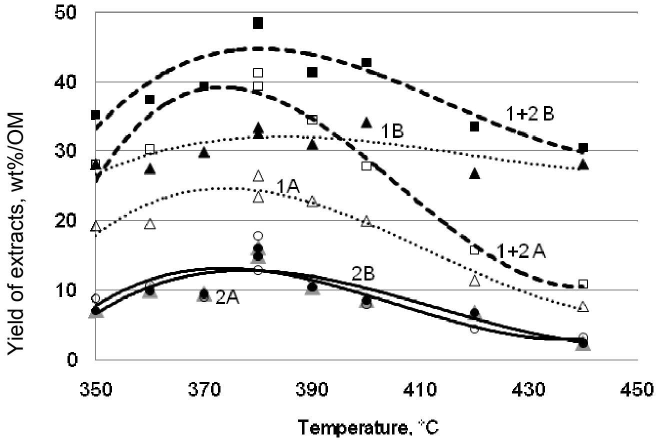


Fig. 3. The comparison of extracts yield for GOS determined by variant A (unfilled marks, 1 – hexane soluble, 2 – benzene soluble and 1+2 – their sum) and those determined by variant B (filled marks).

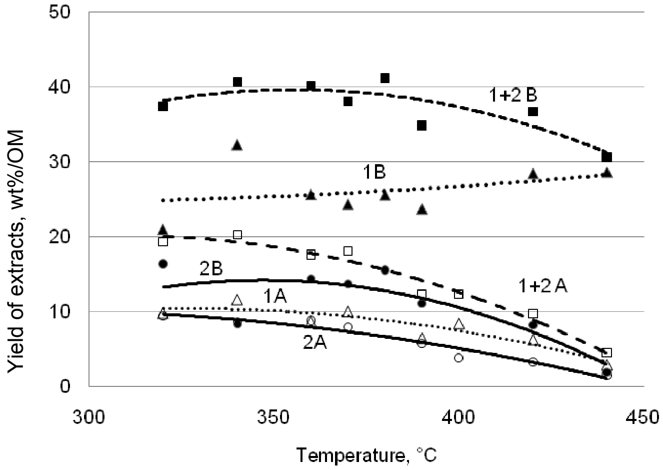


Fig. 4. The comparison of extracts yield for terebinth berries determined by variant A (unfilled marks, 1 – hexane soluble, 2 – benzene soluble and 1+2 – their sum) and those determined by variant B (filled marks).

Hydrous pyrolysis of initial objects

Recently sub/supercritical water has attracted more attention because the process is environmentally friendly (nontoxic), and can be carried out at relatively low temperature. Since water is used both as a reactant and as the reaction medium, the feedstock without any pretreatment or drying can be used.

Hydrous pyrolysis of shale and berries was carried out in pyrolysis conditions at which the maximum yield of soluble pyrolysis product was achieved (duration two hours and pyrolysis temperature 380 °C for shale, and 340 °C for berries). The weight ratio of shale or berries and water was 1:2 and 1:3, respectively. The yields of the products obtained are given in Table 4. The results show that SC water affected product yields and composition of extracts derived from oil shale. Thus, the conversion in the medium of SC water led to a decrease in the amount of solid organic residue and hexane soluble extracts, but to an increase in the benzene soluble extracts.

Table 4. **Product yields at dry individual pyrolysis and co-pyrolysis, wt%/OM**

Pyrolysis products	GOS			Berries			Co-pyrolysis		
	Temperature, °C								
	360	380	400	340	360	380	360	380	400
Gas	10.41	14.10	15.82	22.64	24.08	26.40	17.93	20.27	24.34
Hexane extract	27.45	33.00	34.16	32.29	25.66	25.60	29.92	34.82	31.98
Benzene extract	9.92	15.46	8.54	8.40	14.44	15.54	8.29	8.75	7.26
Total extracts	37.37	48.46	42.70	40.69	40.10	41.14	38.20	43.57	39.24
Organic residue	52.22	37.45	41.47	36.66	35.72	32.47	43.88	36.17	36.46

In the case of berries, the amount of organic residue was about 36–47% less than that of dry pyrolysis. The conversion in the medium of SC water led to an increase in both hexane and benzene extracts. The studies mentioned in the relevant literature also support this result. This finding is consistent with the literature data. As given in Table 4, the yield of total extracts did not significantly increase with the increase in water/solid ratio from 2:1 to 3:1.

The yields of gas and total extracts at hydrous pyrolysis of individual objects increased about 8% compared to those at dry pyrolysis, additionally a water-soluble product formed. With increasing water ratio its quantities increased as well.

Co-pyrolysis of GOS and terebinth berries

Dry co-pyrolysis experiments were made at temperatures 340, 360, 380, 400, 420 °C and duration two hours. Of course, water in pyrolysis products comes from inherent moisture and pyrolysis water of feedstocks.

The maximum yields of extracts from individual feedstocks form within different temperature intervals, but for both of them the quantities increase during conversion in water. So, it was decided to study their co-pyrolysis at nearly SC water temperature (374 °C), which is congruent with preferable pyrolysis temperature for oil shale that is 380 °C and duration two hours.

In Fig. 5 two studied possibilities of co-pyrolysis – dry pyrolysis (a) and hydrous pyrolysis (b) are given. When the yield of products from the feedstocks and their blends at used OM ratio gives a convex line, the synergistic effect takes place.

At dry pyrolysis the amount of hexane extract enlarges on the account of benzene extract, the total extract is formed as a sum of extracts from the individual pyrolysis feedstocks.

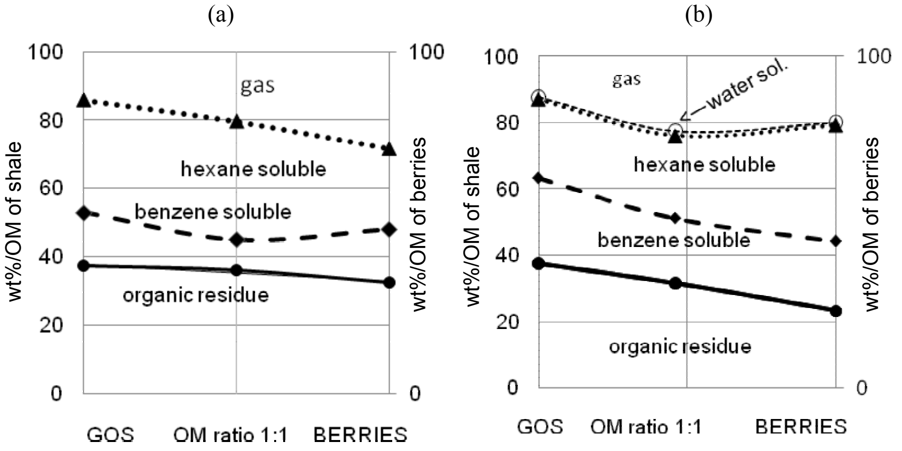


Fig. 5. Distribution of products at co-pyrolysis of Göynük oil shale and terebinth berries: dry (***a***) and in SC water (***b***).

The comparison of product yields from the initial feedstocks and at their co-pyrolysis are given in Table 4 (dry pyrolysis) and in Table 5 (hydrous pyrolysis).

The highest yield (48.46 wt%/OM) of total extract for individual GOS was achieved at 380 °C; the maximum value for berries varied between 40.69 and 41.14%. For gas and organic residue of co-pyrolysis the data for individual feedstocks were summarized. If to summarize the hexane extract yield from individual feedstocks (29.25%) and compare this value with the really obtained yield (34.82%) one can see that 5.57 wt%/OM more of hexane extract was achieved, so an insignificant synergistic effect took place. As for hexane extract yield, synergistic effect was noticed at pyrolysis temperatures 360–380 °C, in which range its values exceed those for benzene extract. At higher temperatures this effect disappears.

Table 5. **Product yields at hydrous individual pyrolysis and co-pyrolysis, wt%/OM**

Pyrolysis products	GOS			Berries			GOS : berries (OM ratio 0.87)
	Water content of mixture, wt%						
	0	67	75	0	67	75	67
Gas	14.10	14.49	15.13	22.95	19.87	20.97	22.40
Hexane extract	33.00	23.77	26.82	31.99	35.02	38.98	24.96
Benzene extract	15.45	27.20	29.72	8.40	21.00	20.08	19.52
Water soluble	–	0.69	0.77	–	0.85	0.94	1.49
Total extracts	48.45	51.66	57.31	40.39	56.87	60.00	45.97
Organic residue	37.45	33.85	27.55	36.66	23.26	19.03	31.63

The temperature dependence of the yield of hexane and total extracts of the initial GOS and its co-pyrolysis with berries is given in Fig. 6, where the increase of hexane extract at blending is evident. Addition of berries to GOS lowers the co-pyrolysis temperature by about 10 °C for reaching the maximum yield of the total extract.

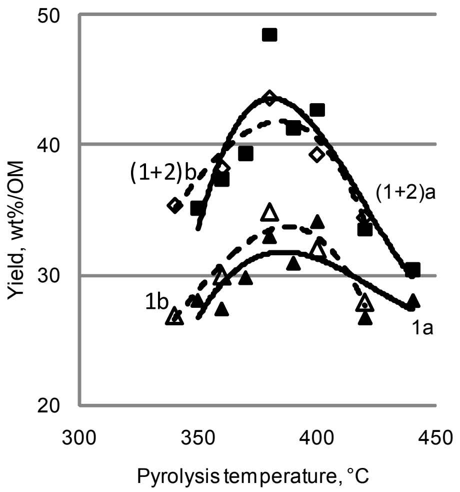


Fig. 6. The temperature dependence of the yield of hexane (1) and total (1+2) extracts at dry pyrolysis (a – continuous line) of GOS and its co-pyrolysis with berries (b –dashed line).

SC water affected product yields and composition of extracts derived from both GOS and terebinth berries. If the amount of water is increased from 67% to 75%, the amounts of all extracts from GOS, including the water-soluble one, are increased; that of the organic residue is decreased. For berries the same tendency, except for the benzene extract, was observed (Table. 5).

The yields of gas, hexane and benzene extracts, and organic residue formed in the SC hydrous co-pyrolysis process and consist of partial contributions of the yields from the initial objects.

As we can see from Table 5 and Fig. 5b, there is no synergistic effect at hydrous pyrolysis of GOS and terebinth berries.

Composition of hexane extracts

The composition of hexane extracts from some experiments was analysed by thin layer chromatography (TLC), the results are given in Table 6. TCL fractions represented nonaromatic (NA), monocyclic aromatic (MCA), polycyclic aromatic (PCA) hydrocarbons (HC), neutral (NHet) and polar (PHet) heterocompounds.

Table 6. **Group composition of hexane extracts, wt%**

Compounds	Initial objects		Hydrous pyrolysis		Co-pyrolysis of GOS and berries	
	GOS, 380°C, 2 h	Berries, 340°C, 2 h	GOS, 380°C, 2 h	Berries, 340°C, 2 h	Dry, 380°C, 2 h	SC water, 380°C, 2 h
NAHC	38.0	6.6	19.6	0.5	33.8	15.0
MCA HC	8.0	0.7	4.1	1.5	4.1	2.9
PCA HC	18.0	5.4	16.1	6.9	19.1	13.5
N Het	18.1	31.9	23.3	31.9	18.4	26.0
P Het	17.9	55.4	36.9	59.2	24.6	42.6

In berries the pyrolysis occurs also *via* an intermediate – primary tar, which thereafter decomposes into secondary oil, charcoal, CO_2 and water [27].

It is clear that extracts derived from oil shale contain mainly nonaromatic and aromatic hydrocarbons in their composition, while extracts from berries consisted of mostly polar heterocompounds. Significant differences between the compositions of extracts obtained by dry pyrolysis and hydropyrolysis were observed. In the case of GOS, the extract of hydrous pyrolysis contained more polar heterocompounds and less nonaromatic HC than that of the initial feedstock. It may be concluded that polar compounds form *via* the reaction between kerogen and SC water. On the other hand, liquefaction of berries in SC water increased the amount of polar heterocompounds, but the hydrous co-pyrolysis increased the content of heterocompounds significantly. The extract of co-pyrolysis consisted mainly of heterocompounds. It should be noted that there is no synergistic effect on the composition of hexane extract in the co-pyrolysis of GOS and terebinth berries. Similar results were also obtained in our previous study related to co-liquefaction of kukersite oil shale and pine wood in supercritical water [26].

The comparison of the extracts' composition shows that GOS, yielding 38.0% nonaromatic HC and 8.0% monocyclic HC, is the most convenient stock for fuel. Although the quantity of hexane extract of GOS increases by hydrous pyrolysis, the content of nonaromatic and monocyclic HC in its composition decreases to 19.6 and 4.1%. Terebinth berries having fatty acids in their composition yield less nonaromatic HC both in hexane and benzene extracts. The hydrous pyrolysis also decreases their content and increases the content of heterocompounds.

Dry co-pyrolysis of GOS and berries enhances the yield of NAHC group from hexane extract – 33.8% from individual GOS 38.00% and 6.6% from berries. So, for searching synergism, the distribution of TLC groups in hexane extract ought to be observed. The yields of TLC groups in wt% from OM of individual samples, their yield in wt% from the total OM of co-pyrolysed samples and the calculated yield (the sum of shares from the individual samples) are given in Table 7. As we can see, a small increase in NAHC group (11.60 wt%/OM against 7.05 calculated) and the decrease in P Het group (8.44 against 12.26 calculated) may be noticed.

Table 7. **The yield of TLC groups of hexane extract from dry individual and co-pyrolysis, wt%/OM**

Pyrolysis products	GOS	Berries	GOS+berries	
			Co-pyrolysis	Calculated
NAHC	12.69	2.12	11.60	7.05
MCA HC	2.68	0.22	1.41	1.37
PCA HC	6.01	1.73	6.56	3.72
N Het	6.04	10.24	6.31	8.28
P Het	5.98	17.78	8.44	12.26

Conclusions

The low-temperature pyrolysis of Turkish Göynük oil shale and terebinth berries as individual objects and their dry and hydrous pyrolysis both individual objects and their mixture in a close system, in an autoclave were studied. The effect of pyrolysis conditions (temperature and duration) on the yield of hexane and benzene extracts was investigated. The composition of extracts was determined by TLC. The maximum extract yields were obtained at 380 °C and 340 °C and duration two hours for GOS and berries, respectively. The obtained results were compared with the data for the open-system pyrolysis.

SC water affected product yields and composition of extracts derived from both GOS and terebinth berries. Although SC water led to a decrease in the amount of organic residue from GOS, the extract of hydrous pyrolysis contained more polar heterocompounds and less nonaromatic hydrocarbon than those of dry pyrolysis. For terebinth berries, the conversion in the medium of SC water led to an increase in the yield of extracts, but they contain more neutral heterocompounds. So, hydrous pyrolysis of single objects increases the yield of extract but deteriorates their composition. The yields of gas, hexane and benzene extracts, organic residue formed in the SC hydrous co-pyrolysis process consist of partial contributions of the yields from the initial objects.

At dry co-pyrolysis the yield of hexane extract increases on the account of benzene extract, the total extract is formed as the sum of extracts from the individual pyrolysis feedstocks. Addition of berries to GOS lowers the co-pyrolysis temperature about 10 °C for reaching the maximum yield of the total extract. Dry co-pyrolysis of GOS with berries resulted in additive rather than in synergistic effect in the total extract yield, but its composition, containing more nonaromatic hydrocarbons and less heterocompounds than that of individual feedstocks, is improved considering its use as a fuel.

If to compare the pyrolysis processes of GOS and kukersite oil shale it can be seen that GOS yields less extract than kukersite, and in both cases their maximum yields are achieved at higher pyrolysis temperature.

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