

## THERMAL ANALYSIS OF CO-FIRING OF OIL SHALE AND BIOMASS FUELS

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**Abstract.** *The effect of co-firing of biomass fuels with oil shale on combustion was investigated. Thermogravimetric analysis and differential scanning calorimetry were the tools used to perform the investigation. Since the combustion of biomass is highly exothermic, biomass fuels can serve as an appropriate fuel feedstock. Biomass fuels producing much volatile matter and containing less cellulose are good candidates for co-firing with oil shale. The biomass samples used in the study were hazelnut shell, wheat bran, poplar, and miscanthus. Co-firing of biomass/oil shale blends was performed using different biomass ratios (10, 20 and 50% by weight).*

**Keywords:** *co-firing, oil shale, biomass, thermogravimetric analysis, differential scanning calorimetry.*

### 1. Introduction

Worldwide there are concerns about limited fossil energy sources in some countries, volatile energy prices, and carbon management. The use of agricultural wastes and non-conventional low-quality fossil fuels can assist in addressing these concerns, especially for the countries having such resources. In various regions of the world, there are many agricultural wastes and, in some areas, there are significant oil shale reserves.

The combustion of some oil shales is problematic due to higher ignition temperature, high ash content, and high emission rates of greenhouse gases. However, biomass is typically characterized by low ash content, neutral

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carbon, low sulfur content, and high reactivity. Blending biomass with oil shale in co-firing applications may be a good method at addressing combustion issues and environmental concerns.

There are many papers on thermal analysis of fossil fuels (coal, lignite, oil shale), biomass fuels, and blends of coal/lignite and biomass fuels; however, no published works were available when we started to study co-firing of biomass and oil shale. This study was designed to fill in this gap.

Research on co-firing fossil and biomass fuels has been carried out mostly on coal basis. They have been focused on both environmental problems and general combustion processes. Two areas lacking in information are: 1) the effect of co-firing on ignition and burnout stages, and 2) additive (i.e., weighted averages or arithmetic averages) and interactive (i.e., synergistic) effects of blends on combustion. There is some disagreement regarding these areas. Some authors report that any quantity of co-fired biomass improves the ignition stage, while others report opposite results. Similarly, some authors have observed that combustion during co-firing is a function of the ratio of biomass to coal (i.e., an additive effect), while others have observed an interactive (i.e., synergistic) behavior in which case the results are not a simple function of the ratio of biomass to coal.

Muthuraman et al. [1] tested the combustion of coal varying the share of wood (5–20 wt.%), using a thermogravimetric analyzer (TGA). They observed an improvement in ignition resulting from lower ignition temperature at lower blend ratios (up to 15 wt.%). However, they observed almost no improvement when using higher blend ratios ( $\geq 15$  wt.% biomass) due to the consumption of oxygen by the biomass because biomass's reactivity is greater. They also observed that the burnout was more complete because of synergistic effect, recorded as changes in the results of derivative thermogravimetry (DTG), and maximum temperatures of the weight loss. Haykiri-Acma and Yaman [2] studied the co-firing of lignite and hazelnut shell (2–20 wt.% of biomass) using TGA. They observed an improvement in ignition/combustion resulting from the maximum burning rates and the temperatures of the maximum burning rates. They also observed an interaction of burnout characteristics of the blends up to 10 wt.% of biomass addition, based on differences in burnouts. However, additive effects were dominant for higher biomass ratios in the blends. Gil et al. [3] studied co-firing of coal and sawdust (5–80 wt.% of biomass) using TGA. They observed that addition of sawdust improved ignition of the blends. However, they did not observe any interaction effects during combustion because no differences between theoretical values and experimental values of the DTG curves were noted. Sahu et al. [4] studied co-firing of coal and biomass chars (10–70 wt.% of biomass) using simultaneously thermogravimetric analysis and differential scanning calorimetry (DSC). Co-firing improved ignition of blends, and some interaction effects during combustion were also established basing on significant differences between theoretical and experimental values of the activation energies of the reactions.

In our work, the combustion behavior of several biomass feedstocks individually and oil shale were investigated. Thereafter, various blends of biomass and oil shale were tested to observe the effect of blending on co-firing performance. The oil shale sample was taken from Ulukışla in the Central Anatolian part of Turkey. The Ulukışla Formation near the town of Niğde is of a lacustrine origin of Paleocene to Eocene Age underlying conglomeratic rocks. Calorific value of the oil shale is typically 2.6 MJ/kg. The biomass samples used in the experiments were oven-dried hazelnut shells, wheat bran, poplar and miscanthus. Hazelnut shells and wheat bran are important agricultural residues for Turkey; poplar and miscanthus are potential energy crops in Turkey because of suitable climate conditions.

### **1.1. Oil shale combustion**

The world fossil energy sources exhibit volatility in both availability and price; hence, non-conventional resources are becoming more popular. Oil shale is one of the non-conventional resources that could be used as an energy source in two different ways. One way to utilize oil shale is retorting. This process converts kerogen in oil shale into synthetic crude oil by pyrolysis or destructive distillation. The resulting oil can be used as a fuel after further processing. An alternative is direct combustion of oil shale to produce power [5].

Direct combustion of oil shale to obtain energy is gaining popularity. At present, about 69% (or 11 million tonnes) of world oil shale production is used for generation of electricity and heat. The utilization of oil shale for retorting, cement production and other purposes are alternative applications. In 2008, generating capacities of countries producing electricity by direct combustion of oil shale were: Estonia (2,967 MW), Israel (12.5 MW), China (12 MW), and Germany (9.9 MW) [6]. In Estonia, pulverized combustion of oil shale is used [7, 8]. Fluidized-bed combustion systems are used in China, Germany, and Israel.

### **1.2. Biomass combustion**

All over the world there are more than 3,000 power plants firing biomass. Their total capacity exceeds 40,000 MW [9–10], individual generating capacities being between 1–80 MW depending on limited availability of biomass fuels within an economical shipping distance [11]. The biomass fuels used are mainly agricultural residues and energy crops.

### **1.3. Co-firing**

One of the advantages of co-firing two different fuel types is that the power plant in operation can burn a supplementary fuel, which, depending on the fuel type and combustion system, can result in little or no additional costs for the new fuel. Co-firing with biomass can be more friendly environmentally because of lower emissions of greenhouse gases from carbon-neutral fuel in

the blend. Co-firing also improves the combustion process of low-calorific fuels by blending them with fuels of higher calorific value [11].

In the last decade, the utilization of biomass in co-firing systems has shown rapid development. Co-firing technology is presently performed on a commercial scale in the USA, Australia, Japan, and in many European countries. There are more than 150 coal-fired power plants in which biomass is co-fired [11]. Generating capacities of these power plants are in the range of 50–700 MW, and the majority being systems firing pulverized coal. Co-firing in plants equipped with pulverized combustion systems will generally require only minor modifications or additions to fuel handling, storage, and feed systems [12].

In our work, the co-firing of biomass and oil shale was investigated. Combustion of most oil shales alone is problematic due to their high ash content, high emissions of CO<sub>2</sub> and SO<sub>2</sub> during combustion, and high ignition temperature. Biomass is typically characterized by low ash content, neutral carbon, low SO<sub>2</sub> emissions, and high reactivity. Therefore, blending biomass with oil shale can enhance oil shale utilization at addressing the combustion issues and environmental concerns.

## 2. Experimental

### 2.1. Analysis of feedstocks

The proximate analysis of the oil shale and biomass samples was made by using a thermogravimetric analyzer. The samples were heated to 110 °C at a heating rate 50 °C/min, in the nitrogen atmosphere, and the samples were held at this temperature for 120 min to determine the moisture content. Thereafter, the temperature was ramped up to 950 °C at a heating rate of 50 °C/min. At 950 °C, gaseous environment was switched from nitrogen to air. At this temperature, the samples were held 120 min isothermally to achieve complete combustion. Proximate analysis results of the fuels are given in Table 1.

A partial ultimate analysis was performed using a LECO TruSpec CHN analyzer. Because of limited quantities of samples available for testing, sulphur content, and hence oxygen content by difference, were not determined. Sulphur content of these feedstocks is typically low and oxygen content typically high [9]. The results of the partial ultimate analysis are given in Table 2.

**Table 1. Proximate analysis of fuels (wt%, as tested)**

Fuel type	Moisture	Volatile matter	Fixed carbon	Ash
Oil shale	7.0	8.4	9.0	75.6
Hazelnut shell	1.5	69.5	28.9	0.1
Miscanthus	2.0	80.5	17.4	0.1
Poplar	1.0	74.0	24.9	0.1
Wheat bran	8.0	65.0	26.8	0.2

**Table 2. Partial ultimate analysis of fuels (wt%, dry)**

Fuel type	C	H	N
Oil shale	3.75	1.05	0.22
Hazelnut shell	50.5	5.63	0.18
Miscanthus	45.2	5.28	0.01
Poplar	46.6	5.71	0.45
Wheat bran	43.2	6.19	2.58

## 2.2. Combustion tests

Combustion tests were performed using TGA and DSC. It was observed that organic matter devolatilized during heating, and, before its combustion started, the quantity of volatile matter increased with heating rate. The heating rate of 50 °C/min was chosen as a reasonable one to prevent the loss of organic matter prior to combustion. Combustion tests in TGA and DSC were performed analogously to that used to determine the proximate analysis data. The combustion tests were made in the air atmosphere. The final temperatures for TGA and DSC experiments were 800 °C and 600 °C, respectively.

In all tests the sample weights were between 2 and 4 mg and particle size in the range of 0.2 mm to 0.5 mm. Small sample size and open pans were preferred in order to promote diffusion of the air during the test. TGA and DSC provide information on oxidation rates from ignition to completion of burning. The data are especially useful for equipment designers to assist them in determining the type and size of furnace, the type and arrangement of burners, and the type of heat transfer surface adjacent to the burners. They also help the designer to determine the amount of fuel for stabilizing ignition at firing pulverized fuel [13].

TGA curves were taken to determine and calculate activation energies, reaction mechanisms, kinetics, and thermodynamics of the chemical reactions. The TGA used in the study was a Perkin Elmer 7.

DSC measures the difference between the heat flow from the sample and a reference as a function of temperature or time. Ignition temperature, burn-out temperature, reaction intervals, and exothermic and endothermic regions can be determined by DSC. The apparatus used in this study was a Mettler Toledo DSC1 of the heat-flux type.

## 3. Results and discussion

### 3.1. Ignition temperature

Ignition temperature is the temperature at which exothermic reactions begin. In our work the ignition temperatures are defined as the first point of the exothermic region of DSC curves. The data for each fuel are given in Table 3. Addition of biomass markedly improved the combustion of oil shale by lowering the ignition temperature.

### 3.2. Burnout temperature

Burnout temperature is the temperature at which combustion or exothermic reactions end. It must be considered at choosing the dimensions of a furnace to burn the fuel completely. Any changes in this temperature may adversely affect combustion efficiency. The burnout temperatures of each fuel type are given in Table 3. The addition of biomass increased the burnout temperature of the blend, however, for biomass addition exceeding 50 wt.% there was little or no effect observed. A tabulation of ignition and burnout temperatures of blended fuels was made by Muthuraman et al. [1] to observe the change of temperatures with blend ratios, and they observed that burnout temperatures of blends were affected by the initial fuel burnout characteristics.

### 3.3. Activation energy

Activation energies for combustion of each fuel were calculated using the Coats & Redfern kinetic method. When the sample size is small and excess air rate high, combustion process is independent of oxygen concentration, and therefore one may assume that oxidation can be described by the first-order kinetics. The data are given in Table 3 and also presented in Fig. 1. There is a clear effect of blending on activation energies. The activation energy ( $E_a$ ) decreases with the increase of biomass amount in the blends. This improves combustion at co-firing the biomass with oil shale. At biomass addition rates exceeding 50 wt.%, ignition temperatures of the blends approach those of the biomass parent fuels indicating that the biomass strongly influences the combustion stage.

**Table 3. Ignition and burnout temperatures and  $E_a$  values of fuels and their mixtures with oil shale**

Fuel type	Ignition temperature, °C	Burnout temperature, °C	$E_a$ , kJ/mol
Hazelnut shell alone	271	539	31.2
50%	288	537	35.8
20%	303	528	57.7
10%	305	519	74.8
Miscanthus alone	300	567	57.6
50%	306	548	66.1
20%	311	537	86.9
10%	325	492	112.7
Poplar alone	295	530	42.1
50%	296	530	61.1
20%	321	500	71.9
10%	325	450	76.6
Wheat bran alone	295	600	45.3
50%	296	600	49.9
20%	308	544	52.6
10%	310	537	64.3
Oil shale	325	425	125.0

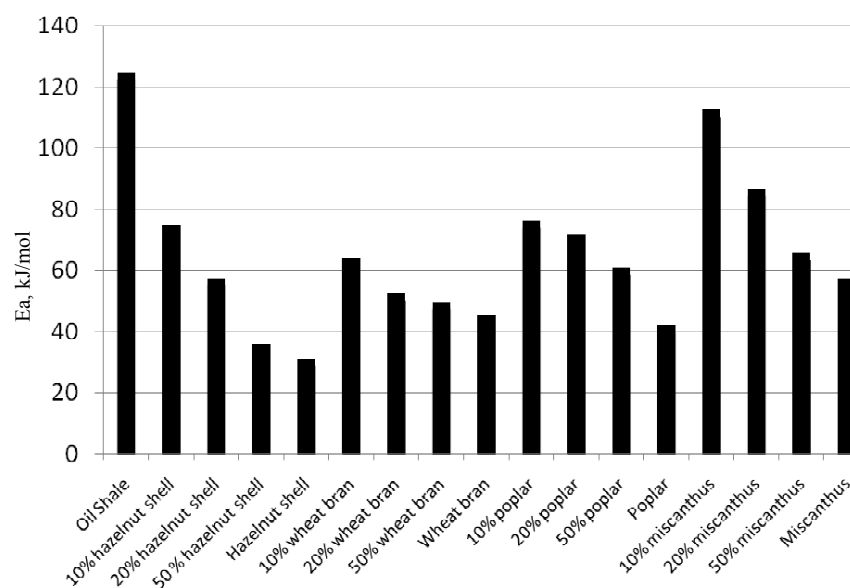


Fig. 1. Activation energies of fuels.

### 3.4. TGA and DSC curves

In Fig. 2, TGA curves of oil shale, biomass fuels, and their blends are provided. DSC curves are given in Fig. 3. The additive effect caused by biomass fuels on oil shale is obvious. Combustion of biomass is a highly exothermic process compared to oil shale combustion.

### 3.5. Model compounds of biomass

Biomass fuels are chemically complex polymeric lignocellulosic materials. They are composed of cellulose, hemicelluloses, and lignin with cellulose and hemicellulose tightly bound to lignin. These compounds and their arrangement in the plant determine physical and chemical properties of the biomass fuels. To investigate possible relationships between these compounds and combustion behavior of biomass fuels, model compounds were analyzed. Their ignition temperatures and burnout temperatures obtained from DSC and TGA tests performed at a heating rate of 50 °C/min are given in Table 4. In our study, the model compounds tested were CF11 fibrous cellulose powder and xylan (hemicellulose) from birchwood, provided by Whatman Company, and loblolly pine lignin, provided by the College of Agricultural Sciences at Penn State University.

The results in Table 4 indicate that biomass fuels with higher hemicellulose and lignin content and lower cellulose content are the most suitable fuels to decrease the ignition temperature of blends with oil shale. Ignition temperature of cellulose is much higher than that of other model compounds of biomass. Similar observations were made by other researchers [14].

A primary reason why ignition and burnout temperatures of biomass fuels differ is their varying lignocellulosic content.

**Table 4. Ignition temperatures and burnout temperatures of model compounds of biomass**

Model compound	Ignition temperature, °C	Burnout temperature, °C
Cellulose	390	590
Hemicellulose	257	516
Lignin	285	612

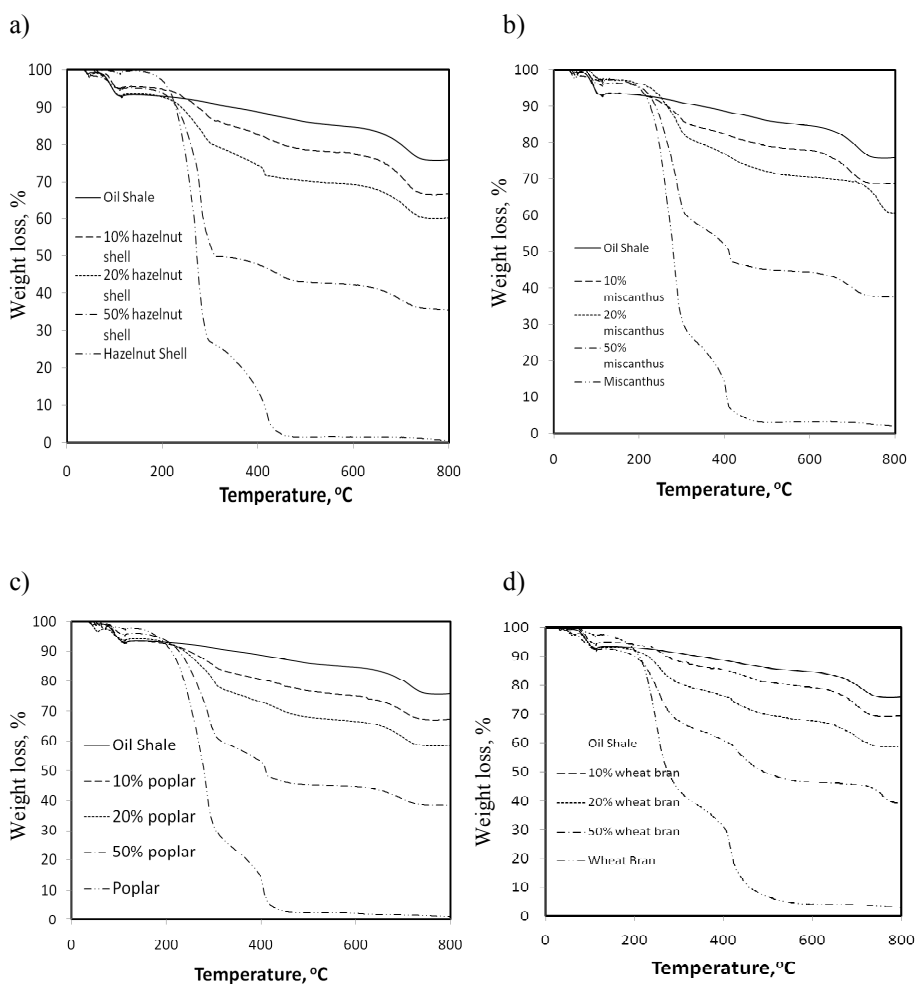


Fig. 2. TGA curves of individual fuels and blends with oil shale: (a) hazelnut shell, (b) miscanthus, (c) poplar, (d) wheat bran.



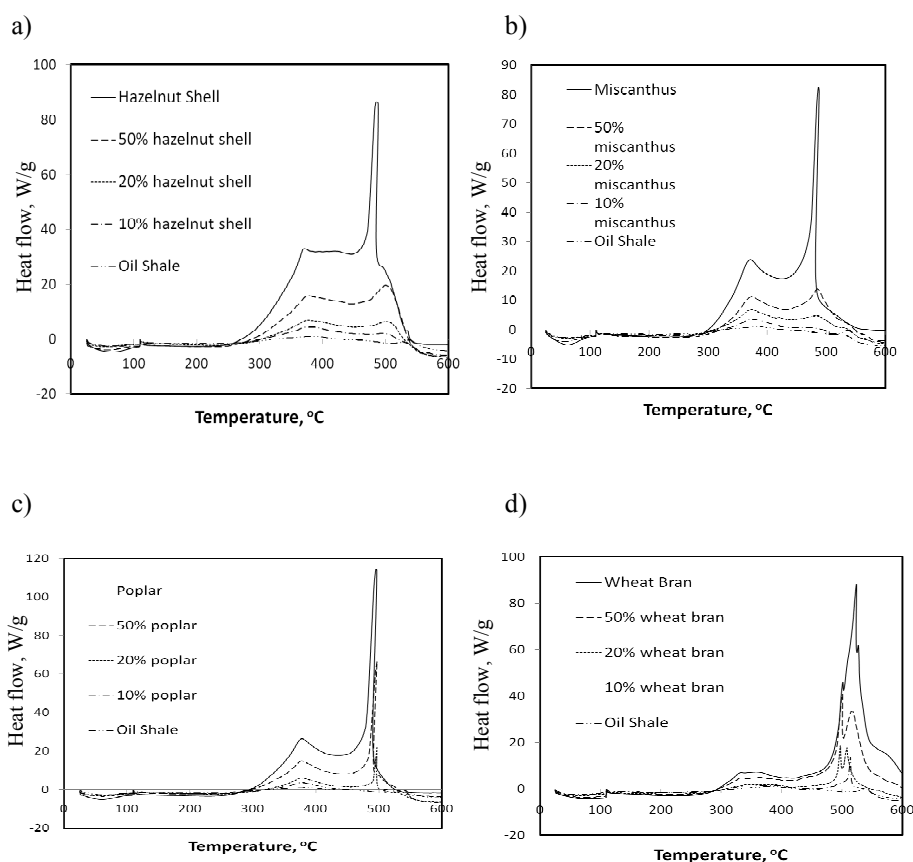


Fig. 3. DSC curves of individual fuels and blends with oil shale: (a) hazelnut shell, (b) miscanthus, (c) poplar, (d) wheat bran.

### 3.6. Additive effect or interactive effect

To investigate if there is any interactive effect between oil shale and biomass fuels during combustion, differences between theoretical and experimental values of the ash content of each blend were compared, following an analogous procedure performed by others [2]. Theoretical values of the individual fuels, oil shale, and biomass/oil shale blends were calculated. The calculation is based on the individual fuels' experimental values using an arithmetic average method to determine the blends' theoretical value for ash content. The experimental and theoretical values for the ash content of each blend and the difference between these results are tabulated in Table 5. The differences remain below 5% except for one value. Differences would be expected since solid fuels are not homogeneous. Also, reproducibility tests were performed, and a deviation of 3–4% was observed for the experimental results (ash content, ignition temperature, and burnout temperature). Thus, it

was not clear whether synergistic interactions occurred between two oil shale and biomass samples (i.e., hazelnut shell and poplar). Most likely heterogeneity of the samples and small sample size were the primary reasons why no definitive conclusions can be drawn.

The same procedure was also performed for determination of activation energy. Activation energies of the blends were much lower than expected basing on theoretical arithmetic averages. The experimental and theoretical values for the activation energy of each blend and differences between the results are given in Table 6. The results indicate a positive interaction for the co-firing scenario. However, this result differs from that for ash content. This is probably due to a short interaction period when combustion starts (the point at which activation energies were calculated) followed by a less reactive period during which char combustion occurs [15].

**Table 5. Deviations between theoretical and experimental ash content**

Added fuel, %	Ash content (theoretical)	Ash content (experimental)	Deviation, %
Hazelnut shell	10	68.13	-2.39
	20	60.56	-0.92
	50	37.85	-6.21
Wheat bran	10	68.14	1.26
	20	60.58	-3.27
	50	37.9	3.43
Poplar	10	68.13	-1.51
	20	60.56	-4.23
	50	37.85	1.72
Miscanthus	10	68.13	0.54
	20	60.56	0.23
	50	37.85	-0.92

**Table 6. Deviations between theoretical and experimental activation energy values**

Added fuel, %	Activation energy (theoretical)	Activation energy (experimental)	Deviation, %
Hazelnut shell	10	115.6	-35.3
	20	106.2	-45.7
	50	78.1	-54.2
Wheat bran	10	117.0	-45.1
	20	109.1	-51.8
	50	85.2	-41.4
Poplar	10	116.7	-34.4
	20	108.4	-33.7
	50	83.6	-26.9
Miscanthus	10	118.3	-4.7
	20	111.5	-22.1
	50	91.3	-27.6

#### 4. Conclusions

Direct combustion of solid biomass and oil shale is a method of optimal utilizing these solid fuels. Co-firing oil shale with various biomass fuels was investigated by TGA and DSC varying biomass proportions in blends. Both methods can simulate the conditions at pulverized combustion of oil shales. Solid fuel combustion is primarily governed by its ignition and burnout temperatures, which are, besides being decisive in the combustion process, also crucial for designing the combustion equipment.

Blending of oil shale with biomass lowers the ignition temperature and improves the combustion process. Since biomass contains much oxygen and volatile matter, it is easier to ignite the blended samples than oil shale alone. Activation energies at combustion of blends are less than theoretical values calculated on the basis of arithmetic averages determined for individual fuels. This indicates a positive interaction in the reduction of activation energy during combustion. However, the same level of synergism was not observed when comparing ash content of the blends and their theoretical arithmetic averages basing on ash content of individual fuels. This is probably due to a short interaction period at the start of combustion, followed by a less reactive period during which char combustion takes place.

Biomass and oil shale can be co-fired in existing pulverized-firing systems. Since the combustion of biomass is highly exothermic, biomass fuels can serve as an appropriate fuel feedstock. The selection of a biomass fuel for co-firing systems can be done basing on the content of cellulose, hemicellulose, and lignin in biomass, since combustion behavior depends on the proportion of these compounds. Biomass fuels producing much volatile matter and containing less cellulose are good candidates for co-firing with oil shale.

Biomass (10% and 20% by weight) blended with oil shale, is a good option for co-firing owing to formation of a sufficient amount of volatile matter to maintain stability in ignition and combustion.

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