Current status of co-pyrolysis of oil shale and biomass

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Abstract. *The use of biomass (BM) and oil shale (OS) blends for the production of cleaner and improved fuels and chemicals through co-pyrolysis has recently attracted attention. The potential benefits, synergetic effects, interactions and promotion and inhibition effects of co-pyrolysis of BM and OS are reviewed and analyzed in this article based on an overview of various recent studies of co-pyrolysis, including the experimental and operational parameters and the yield and composition of the products. The effects of co-pyrolysis on different feedstock blends are discussed to guide future research on BM and OS co-pyrolysis. The effects of different pyrolysis parameters that can improve the pyrolysis process and quality of products are also reviewed. These parameters include CO_2 and steam atmospheres, heating rate, reaction temperature and particle size. Overall, in most cases reviewed, co-pyrolysis can enhance the yields of bio-oils, producer gas and chars as well as improve their properties while reducing the environmental effects of fossil fuels.*

Keywords: *oil shale, biomass, co-pyrolysis, gas atmosphere, operational parameters.*

1. Introduction

The current accelerating increase in energy consumption, shortage of natural resources, environmental pollution and depletion of conventional fossil fuels around the world have urged the research and implementation of clean, alternative and renewable sources for energy generation and production of fuels [1, 2]. The use of conventional fossil fuels as a source of energy and petrochemical products has increased the emissions of CO_2 significantly and altered the carbon balance on Earth [3, 4]. A promising economically feasible and cleaner alternative to the production of improved biofuels and chemicals is the co-pyrolysis of carbon-neutral fuels, such as biomass (BM), and alternative fuels, such as oil shale (OS) [5–7].

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Oil shale is a sedimentary rock found in different geological formations, which is composed of organic matter, ash and inorganic matter. OS is considered an alternative fossil fuel whose organic matter (kerogen) can be converted into oil and gaseous products, such as shale oil and shale gas, through different processes, including pyrolysis, combustion, gasification and liquefaction under supercritical conditions [8–11]. There are OS deposits in many regions of the world, exceeding the crude oil reserves [12, 13] and making OS one of the most important alternative fossil fuels. The United States has the largest proven reserves, but OS can also be found in Brazil, China, Russia, Estonia, Jordan, Morocco, Australia, Canada, Italy and Congo [14–16]. Pyrolysis is one of the most frequently used technological processes for the retorting of OS, and it is used to convert the organic matter kerogen into bitumen and bitumen into shale gas, shale oil and semicoke [17, 18]. There are still various challenges in the OS conversion process and the usage of its products. Some of these challenges include reducing the environmental effects, improving the quality and composition of the products [19, 20] and reducing the yields of solid residues.

Biomass is a renewable, carbon-neutral resource with the potential to supply approximately 14% of the world's energy consumption [21–23], making it one of the most important energy sources of its kind. BM can decrease the dependence on fossil fuels [24, 25], as well as emissions of CO_2 and other pollutant gases [26]. Owing to its different characteristics, such as high volatile matter content and low ash content [27], BM can be processed into bio-oil, biogas, char and activated carbons, among other products [28]. Thermochemical, biochemical and mechanical conversion processes are the most commonly used processes for BM conversion [29, 30]. Among the thermochemical processes, pyrolysis has been widely used to convert BM into products because of the favorable conditions for converting solid carbonaceous feedstock (FS). However, the obtention of BM products from individual pyrolysis still needs further improvement and research owing to technical and economic challenges, such as low calorific values and high moisture content [31].

Pyrolysis is a thermochemical conversion process in which FS undergoes thermal degradation in the absence of oxygen, breaking large molecular structures and producing gas, liquid oil and solids [32, 33]. High-heating-value liquid oils obtained through pyrolysis are used in furnaces, turbines, engines, and the petrochemical industry [34]. Other products obtained from pyrolysis are high energy content gases used for heat and power generation [35], and high carbon content and adsorbent chars. Pyrolysis can also be an intermediate process, as it is a part of other thermochemical conversion processes, such as gasification and torrefaction. The yields and composition of products obtained from pyrolysis depend on different parameters, including the type of FS and its physical and chemical composition (organic and mineral content, particle size, moisture content, heating value), the reactor used, and the operational

parameters, such as reaction temperature, heating rate, residence time and gas atmosphere (N_2, CO_2, H_2O, H_2, CH_4, CO_2).

Co-processing of FS has been studied to analyze the interactions between fuels, improve the quality of fuel and reduce its environmental impact, thus producing improved and cleaner liquid and gaseous fuels [36]. Co-pyrolysis is a process in which the thermal degradation of two fuels occurs through a set of chemical reactions, heat and mass transfer mechanisms, and interactions between the fuels [37]. The yield and composition of liquid, solid and gaseous products obtained from co-pyrolysis cumulatively depend on the products from individual pyrolysis, the synergetic effects that may promote or inhibit the yield and quality of the products, the interactions between the organic and mineral matter of both fuels, and the operational parameters [38].

This work aims to present different developments, findings and advancements in BM and OS co-pyrolysis processes. Various studies are reviewed and compared. First, an overview of the most relevant operational parameters used for each co-pyrolysis experiment is provided, followed by a presentation of the main findings, improvements, synergetic effects, interactions, and characteristics of the products obtained from co-pyrolysis of different feedstocks. The present study also reviews the main operational parameters of OS pyrolysis, including the effects of the gas atmosphere, heating rate, particle size, and reaction temperature.

2. Overview

2.1. Individual pyrolysis of oil shale and biomass

Through different industrial retorting processes, OS has been used to obtain shale oil, shale gas and semicoke with different yields (5–20 wt% of shale oil, 5–20 wt% of shale gas and > 60 wt% of semicoke) and compositions. The yields of products depend, among other factors, on the type of OS, the retorting reactor used and the operational parameters [39]. Different OS types from various worldwide regions give different product yields, as the organic matter and lower heating value (LHV) in OS can vary from 5 to 80% [40] and from 5 to 20 MJ/kg, respectively. OS retorting processes have been studied to improve the quality and increase the yield of usable products [4, 19, 41]. However, there are still different issues to be resolved from the individual retorting of OS. For instance, semicoke, as a product of OS retorting, is sent to landfills. Additionally, the high molecular weight, viscosity, nitrogen and sulfur content, along with the low stability of shale oil, can cause environmental effects (emission of NO_x and SO_x) [42–44] and may require further improvement and refining of the oil [19, 20]. Moreover, the individual retorting of OS can produce high amounts of polluting gaseous carbon, such as CO_2, leading to environmental contamination.

Biomass has been widely used to produce bio-oils, semi-coking products, fuels, chemicals and petroleum substitutes [45]. The yields of products obtained from BM pyrolysis vary depending on the type of pyrolysis process used, such as torrefaction, carbonization, conventional pyrolysis, fast pyrolysis and flash pyrolysis. Conventional pyrolysis yields approximately 50 wt% of liquids, 20–25 wt% of gas and 20–25 wt% of solids. Fast and flash pyrolysis yields up to 75 wt% of liquids, less than 20 wt% of gas and 13–25 wt% of solids [6]. However, the individual pyrolysis of BM still poses different challenges, such as the low energy density (10–40% of that in most fossil fuels), high moisture content and low heating value of BM (15–19 MJ/kg) [5, 46]. As a resource, biomass is highly diverse; the different types of BM significantly differ in composition, making the characterization of the matter a challenge and requiring individual techniques for the pretreatment and processing of its various types [47]. For some types of BM, FS availability is a constraint in specific regions or due to seasonal and environmental conditions, leading to challenges in transporting the types of BM available and limiting their use in specific locations and environments [48]. The properties and quality of the products obtained from BM pyrolysis can also challenge their usage. Products such as bio-oil can have undesirable properties, including high corrosiveness, thermal instability and a variable composition of the bio-oil depending on the type of BM and pyrolysis conditions [49]. As with shale oil, bio-oil needs refining and upgrading to use it as a fuel and make it compatible with current energy conversion technologies. Moreover, the application of BM pyrolysis is usually economically and technologically limited to prototype and small-scale processes [50]. The individual pyrolysis characteristics and products obtained from BM conversion have been widely studied [51–53].

2.2. Co-pyrolysis

Co-pyrolysis has been studied to enhance the properties and products of individual pyrolysis. BM has been used in co-pyrolysis to decrease the consumption of fossil fuels, reduce environmental problems, such as the CO_2 emissions and pollutant gases (H_2S, NO_x, SO_x) produced from conventional usage of solid fuels [45, 54], and address operational challenges in processing fuels, such as the fused-ash slagging that forms inside reactors [55]. The differences in the composition of BM, including the fraction of oxygenated species, H/C and O/C ratios, ash composition, and volatile matter [56, 57], can potentially promote beneficial synergetic effects and interactions during co-pyrolysis. Other possible positive effects include reducing pollutants from solid fossil fuel conversion, improving the product yields and composition, and enhancing the thermal reactivity of the fuels [58, 59].

Various studies have been conducted on the co-pyrolysis of BM and other fuels, including switch grass, rice straw, sawdust, crystalline cellulose and lignin with bituminous coal [60–62], olive stone, wheat straw, almond shells

and pine sawdust with coal [63], corncob wood waste, wheat straw, rice straw, sawdust and pine with subbituminous coal [64–69], and corncob and hazelnut shells with lignite [59, 70]. Plastics have also been co-pyrolyzed with BM, resulting in improvements in the properties of pyrolysis products while using plastic residues as an alternative. Plastics, for example, have been used to upgrade hydrocarbon mixtures [35, 71] by donating hydrogen and increasing the quality and yield of bio-oil [72, 73]. Some studies using plastics include those by Jin et al. [32] on the synergetic effects in the co-pyrolysis of wheat straw and polyurethane, and by Özsin and Pütün [37] who conducted kinetic studies of the co-pyrolysis of cherry seeds and polyvinyl chloride. Further, co-pyrolysis of BM and OS with residues such as waste tires and sewage sludge can produce a valuable, improved bio-oil while reducing the amount of waste that creates environmental problems and health risks as these residues are non-biodegradable or require a challenging waste recycling process [74–77]. Moreover, the individual pyrolysis of waste produces extensive amounts of ash and produces gas-rich CO_2 with a low heating value [78]. Co-pyrolysis can use waste and residues while producing usable products such as bio-oil. A relevant example is the co-pyrolysis of sewage sludge and wheat straw investigated by Wang et al. [27].

2.3. Effects of co-pyrolysis

Several positive effects have been observed in the quality and yield of products from co-pyrolysis due to interactions and synergetic and catalytic effects between the FS blends. FS with a high hydrogen content and high H/C ratios, such as BM and plastics, can play an essential role in co-pyrolysis, acting as hydrogen donors and promoting FS decomposition and cracking of fuel blends, which can increase the yield of oil and decrease that of solids [59, 60, 62, 66–68, 70]. The alkaline and alkali earth metals present in different feedstocks, such as BM, plastics, tires and sewage sludge, can act as catalysts and enhance the co-pyrolysis process, therefore increasing the fuel conversion and yields of usable products and promoting secondary cracking and dehydrogenation. FS ash can also have similar catalytic effects in co-pyrolysis [27, 32, 66, 67].

For example, BM in co-pyrolysis can promote the solids decomposition and increase the co-pyrolysis decomposition rate because of its high volatile content and low fixed carbon, resulting in higher yields of gas and oil and lower yields of solid products [60–62, 64, 69]. Co-pyrolysis using BM can also produce a gas with a higher concentration of CO, as the CO_2 produced can react in the Boudouard reaction between char and CO_2, increasing the yield of CO and decreasing that of CO_2 [67, 68]. Co-processing can also shift the pyrolysis temperature and reduce the activation energy of the blend [37, 60, 65]. Co-pyrolysis using BM, plastics and tires, among other materials, can improve the fuel properties of oil. Some improved properties include lower water and oxygen content, higher calorific value, higher carbon and hydrogen content [32, 74], lower fractions of heavy aromatics and heterocyclic compounds, and higher fractions of light tars and light aromatic tars [32, 61].

However, the synergetic effects of co-pyrolysis could not be generalized. Several studies have observed a promotion or inhibition effect on the yield of products, including the yield of oils, gas, non-condensable gases and solids [64, 67, 68]. Some studies have found inhibitory effects on the pyrolysis rate and activation energy due to a decrease in the heat transfer, while other studies have proved the promotion effects on the oil yield, a decrease in the solids yields as well as in the reaction temperatures [32, 37, 62]. The synergetic effects have also been observed to depend on the blend mixture ratio and reactor type. For example, co-pyrolysis in fluidized- or fixed-bed reactors has shown improved synergetic effects, unlike that in Thermogravimetric Analysis (TGA) [27], while higher pyrolysis temperatures (> 500 °C) favor interactions between feedstocks [63, 69]. Other studies have found that co-pyrolysis products behave as additive products from the individual pyrolysis of FS, indicating no synergetic effects [65, 70].

Although co-pyrolysis has many advantages and positive effects, various challenges must be considered. For example, many experimental data from co-pyrolysis have been obtained from pilot-scale equipment and TGA [65]. Co-pyrolysis can also cause technical and operational issues and require modifications to the power plants to operate them with FS mixtures, thereby reducing the generation capacity [63]. However, these modification costs can be compensated for by the decrease in fuel cost when using BM, residues or waste [70]. The modifications required for pyrolysis plants to operate in co-pyrolysis require fewer investments than new plants for individual pyrolysis of renewable FS, such as BM, or waste, such as plastic residue [65].

2.4. Oil shale and biomass co-pyrolysis

Co-processing of OS and BM has the potential to reduce various challenges from individual pyrolysis while producing higher yields of bio-oil with improved composition [60]. BM for char, oil and gas production is pyrolyzed at temperatures of 350–500 °C, which are within the same temperature range of OS retorting [79]. The bio-oils obtained from BM pyrolysis have very different characteristics from those of shale oil. For example, bio-oil is lighter than shale oil and contains more oxygenated compounds [80]. It is mostly water-soluble differently from the mainly benzene-soluble shale oil [81]. Co-processing of BM and OS is a promising option for improving the retorting of OS, bettering its pyrolysis characteristics and providing environmental benefits such as the reduction of CO_2 emissions [81, 82]. The different characteristics of BM, OS and their pyrolysis products have been discussed as possessing potential synergetic effects, resulting in improved co-pyrolysis products. However, these synergies are not generally the same in all cases and have been observed to depend on the type of BM [82], reactor, fossil fuel and pyrolysis conditions [83]. Table 1 presents the main operational parameters used in various studies on the co-pyrolysis of BM and OS.

Table 1. Experimental operational parameters used in the studies on oil shale and biomass co-pyrolysis

Biomass	Oil shale	Experiment type	Temperature range, °C	Heating rate, °C/min	Residence time	Atmosphere	Sample mass	Particle size, mm
E. rigida (flowering plant) [19]	Syitomer (Turkey)	TGA	25–1000	10	–	0.1 l/min N_2	5–15 mg	BM 0.425-1.250, OS 0.425-0.600
		Fixed bed reactor	450, 500, 550	10	–	0.1 l/min N_2	–	
Spirulina (algae) [84]	Fushun (China)	TGA	20–950	20, 30, 40, 50	–	0.08 l/min N_2	5 mg	< 0.177
		Py-GC-MS	–	20 °C/ms	20 s	N_2	0.5 mg	
Terebinth berries [81]	Goynuk (Turkey)	Autoclave	340, 360, 380, 400, 420	100 min heating time	120 min	Dry pyrolysis Hydrous pyrolysis 4 and 6 ml	4 g	< 0.120
Spent mushroom [82]	Huadian (China)	TGA	25–750	10	–	0.05 l/min N_2	8 mg	< 0.9
		Retorting reactor	490, 590	–	–	0.2 l/min N_2	50 g 0.52 g/min	
Wheat straw grain [80]	Huadian (China)	Cylindrical retort	520	10	20 min	0.3 l/min argon	24 g	< 3
Wood pellet [79]	Huadian (China)	Bubbling fluidized bed reactor	430, 460, 490, 520, 550, 600	–	–	N_2	100 g (feeding speed 24.3 r/min)	3
Pine sawdust [83]	Kukersite (Estonia)	Autoclave	360, 380, 400	–	60, 120, 180 min	–	10 g	BM < 1.0, OS < 0.1
Pine and spruce [39]	Kukersite (Estonia)	Fischer assay	25–520	5	–	–	50 g	0.04-0.10
C.vulgaris Microalgae [85]	Guandong Maoming (China)	Quartz tube reactor	500, 600, 700, 800, 900	–	15 min	0.08 m³/h N_2	0.2 g	< 0.2
Alkaline lignin [86]	Tongchuan (China)	TGA	30–900	30	–	0.05 l/min N_2	–	< 0.074

"–" data not available

2.4.1. Effect of synergy

Co-pyrolysis can promote the yield of products through synergetic effects owing to the interactions between OS and BM. In various studies, these interactions resulted in non-linear changes in yields, unlike the linear changes in yields from the individual pyrolysis of FS. The interactions also increased the yield of oil and its H/C ratio, as observed by Chen et al. [79], and the yield of gas while reducing that of solid residues [80, 82, 84–86]. The synergetic effect of co-pyrolysis can depend on the blend ratio of BM:OS, as shown by Dai et al. [84], who demonstrated a maximum synergy at 30 wt% blends of OS using microalgae and OS. The synergetic effects were also observed to reduce the activation energy of the mixtures, which decreased mainly at low temperatures (< 400 °C). This was observed by Chen et al. [80] and Dai et al. [84] in the co-pyrolysis of OS with wheat straw grain and microalgae, respectively. However, the synergetic effects noticed in co-pyrolysis cannot be generalized, as a study by Kiliç et al. [19] with OS and *E. rigida* and that by Janik et al. [81] with OS and Terebinth berries found that co-pyrolysis behaved as an additive process, resulting in additive yields of products from the individual FS pyrolysis. Though, a study by Johannes et al. [83] with pine sawdust and OS has described minimal synergetic effects and only at the initial stage of decomposition.

2.4.2. Effect of BM:OS blend ratios

The blend ratio of BM:OS was also seen to affect the product yields and composition and thermal decomposition, with an accelerating or delaying effect on the decomposition and a change in the activation energy of the process [19]. Chen et al. [80] used wheat straw grain and OS, proving that higher wheat straw quantities in the blend with OS increased the yields of oil and semicoke unlike those from the individual pyrolysis of OS. For microalgae and OS, higher OS amounts delayed thermal decomposition [84]. A study by Chen et al. [79] on wood pellets and OS blends showed that BM:OS ratios of 3:1 and 1:1 resulted in a decrease in oil yield (from 19.7 wt% for pure OS to 10–13 wt% for BM:OS ratios of 3:1 and 1:1), inhibition of the production of heteroatomic hydrocarbons and promotion of that of unsaturated hydrocarbons. For the alkaline lignin and OS co-pyrolysis studied by Bai et al. [86], a small amount of alkaline lignin promoted OS pyrolysis. It produced more methane by breaking the main covalent bonds of OS. In addition, at higher alkaline to lignin ratios, the promotion effect was significantly reduced. The co-pyrolysis of microalgae and OS carried out by Hu et al. [85] established that with higher BM quantities, the pyrolysis process was postponed while increasing the yields of H_2 and CO, as well as the heating value of gas, and decreasing the solid residues yield from 41.50 wt% at 1:9 BM:OS to 22.55 wt% at 1:1 BM:OS.

2.4.3. Catalytic effect

Different elements present in BM and OS can potentially act as catalysts, promoting the pyrolysis and decomposition of FS and increasing the yields of oil and gas. These elements include alkali and alkaline earth metals, and inorganic non-metallic elements which in BM express a promotion effect and in OS ash an inhibition effect. Dai et al. [84] discovered that during the co-pyrolysis of microalgae and OS at 400 °C, the ash alkaline earth metals present in the FS ash had a catalytic effect, being revealed by the enhancement of the decomposition of organic matter, promotion of the carbonization process and increase of the aliphatic hydrocarbons fraction from 9.57 to 17.48%. In the co-pyrolysis of spent mushroom and OS, Jiang et al. [82] noted that alkali and alkaline earth metals (e.g., potassium) in BM produced a catalytic effect on the decomposition of OS, improving its pyrolysis characteristics. While studying the co-pyrolysis of microalgae *C. vulgaris* and OS, Hu et al. [85] established that the solid residues of BM acted as catalysts, promoting the production of gas and oil from OS. However, the ash particles in OS inhibited the production of oil and gas in the microalgae.

2.4.4. Hydrogen content

The higher hydrogen content of BM contributes to the participation of hydrogen-free radicals in co-pyrolysis, which can increase the oil yield and promote the cracking of kerogen and bitumen, resulting in oil with a higher H/C ratio. Chen et al. [80] found that in the co-pyrolysis of wheat straw grain and OS, the hydrogen-free radicals present in BM contributed to cracking the bridge bonds in kerogen, leading to a higher H/C in the oil obtained. Bai et al. [86] discovered that in the co-pyrolysis of alkaline lignin and OS, the early decomposition of the former promoted the pyrolysis of OS, providing hydrogen-free radicals and producing more CH_4.

2.4.5. Yields and composition of products

The composition of products can be affected by OS-BM co-pyrolysis, resulting in products with additive compositions or enhanced contents of products due to synergetic effects. For oil, the hydrogen and carbon contents increased while that of oxygen decreased. The oil obtained from co-pyrolysis contains lower quantities of heteroatomic compounds and higher amounts of aromatic hydrocarbons as well as higher fractions of intermediate and heavy compounds compared to the oil from individual pyrolyses. For example, the oil from the co-pyrolysis of wheat straw grain and OS contained lower amounts of light compounds and higher quantities of medium compounds, while there was but a slight difference in the amount of heavy compounds between the two types of oil [80]. The oil obtained by Jiang et al. [82] from the co-pyrolysis of spent mushroom and OS had a higher content of carbon and hydrogen and a lower content of oxygen compared to the oil from individual pyrolyses. The product

yields from the co-pyrolysis of OS and BM obtained in different studies are listed in Table 2.

2.5. Co-pyrolysis of oil shale and other feedstocks

Other feedstocks and residues, such as different types of waste plastics or residues from OS retorting, can be used in co-pyrolysis processes with OS. Recycling waste plastics through thermochemical conversion processes, such as co-pyrolysis, is a promising approach for utilizing waste to produce liquid fuels or petrochemical products [87]. Plastics have a high H/C ratio, being similar to that of alkanes, which can produce a liquid fuel with a high H/C ratio [88–90]. Co-processing plastics with other fossil fuels has been proposed to enhance fuel conversion into liquid products, and because of their high hydrogen content, these materials can serve as a hydrogen source in the conversion of OS into improved liquid fuel [91–93]. Moreover, adding plastics to OS makes the processing of the mixture more feasible than converting plastics individually [94]. Different studies have achieved high processing efficiencies [92, 95], but it has also been observed that the feasibility of co-pyrolysis depends on the type of OS, type of plastic used and pyrolysis conditions [93]. Table 3 presents the results of various studies on the co-pyrolysis of OS with plastics and shale oil sludge.

Hong et al. [97] demonstrated synergetic effects in the co-pyrolysis of OS and shale oil sludge from discrepancies in the product yields compared to the additive yields from individual pyrolysis, promoting the solid residue decomposition and gas yield. Other beneficial interactions of co-pyrolysis were observed by Aboulkas et al. [96] using polystyrene and OS. In this study, the decomposition of OS accelerated the weight loss of organic matter, the thermal stability of the co-pyrolysis process increased and the peak rates of mass losses shifted to higher temperatures. In the co-pyrolysis of low-density polyethylene with OS carried out by Tiikma et al. [91], the differences between the experimental and calculated yields proved interactions to take place, as plastics provided hydrogen in the processing of OS and enhanced the oil yield. However, other studies have not found clear evidence of synergetic effects when comparing additive individual pyrolysis products with co-pyrolysis products. This lack of synergy was observed in the case of co-pyrolysis of Kukersite OS and plastics conducted by Alboukas et al. [93], where the differences between the experimental and calculated results were irregular and below the accuracy of the experiments. This was also noted by Bozoglu et al. [92] in the co-pyrolysis of blends of polyethylene (LDPE) and OS where no synergetic effects were observed.

Co-pyrolysis of OS with plastics can improve the quality and yield of products because plastics can act as catalysts in the decomposition of OS, and the yields of oil and gas can increase while the solids yield decreases. Alboukas et al. [93] reported that using OS and different plastics (LDPE,

Table 2. Yields of products from co-pyrolysis of oil shale and biomass

Biomass	Oil shale	Blend ratio BM:OS	Oil yield, %wt	Gas yield, %wt	Water yield, %wt	Solids yield, %wt	Main co-pyrolysis observations
E. rigida [19]	Seyitomer (Turkey)	1:0	25–30	50–55 (water + gas)		15–20	Higher oil yields No synergy*
		1:1	15–20	55–60 (water + gas)		20–25	
		0:1	5–10	40–55 (water + gas)		30–35	
Terebinth berries [81]	Goynuk (Turkey)	1:0	40–41 (total liquid)	22–26	–	32–37	Improved oil quality No synergy
		1:1	38–44 (total liquid)	18–25	–	36–44	
		0:1	37–46 (total liquid)	10–16	–	37–52	
Spent mushroom [82]	Huadian (China)	1:0	9–11	37–40	9–14	36–50	Synergy Higher yields of usable product
		1:1	7–17	24–40	2–4	50–61	
		0:1	7–17	15–20	0–2	65–76	
Wheat straw grain [80]	Huadian (China)	1:0	17	12.5	9	61	Improved oil quality Synergy OS acted as a catalyst
		3:1	18	10	8.5	63	
		1:1	18	8	8	64	
		1:3	19	7	7.5	65	
		0:1	20	5	7	66	

Table 2 (continued)

Biomass	Oil shale	Blend ratio BM:OS	Oil yield, %wt	Gas yield, %wt	Water yield, %wt	Solids yield, %wt	Main co-pyrolysis observations
Wood pellet [79]	Huadian (China)	1:0	8	65	10	27	Improved oil quality Synergy Higher oil yields up to 520 °C
		3:1	10	42	8	40	
		1:1	13	30	6	50	
		1:3	17	20	4	60	
		0:1	20	13	1	67	
Pine and spruce [39]	Kukersite (Estonia)	1:0	16–26	20–21	24–26	28–39	Significant differences in OS and BM pyrolysis oils
		0:1	28	8	6	58	
C. vulgaris Microalgae [85]	Guandong Maoming (China)	1:0		89 (liquid + gas)		10	Synergy Solid residues acted as catalysts Higher yields of usable product
		9:1		78 (liquid + gas)		21	
		7:3		68 (liquid + gas)		32	
		1:1		59 (liquid + gas)		41	
		0:1		30 (liquid + gas)		70	

* Existence of promotion or inhibition effects due to interactions between fuels. Synergy existed in experiments where there was a difference in the experimental and calculated yields of products. Yields displayed are from experimental results.

"–" data not available

Table 3. Experimental parameters of co-pyrolysis of oil shale and other feedstocks

Feedstock	Oil shale	Experiment type	Temperature range, °C	Heating rate, °C/min	Residence time	Atmosphere	Sample mass	Particle size, mm
Low-density polyethylene [91]	Kukersite and Dictyonema (Estonia)	Autoclave	420, 540	–	20–120 min	–	4 g	0.04
Polystyrene [96]	Tarfaya (Morocco)	TGA	20–1000	2, 10, 20, 50, 100	–	0.06 l/min N_2	20 mg	FS 0.1–0.2, OS 0.1
Polyethylene (LDPE) [92]	Goynuk (Turkey)	TGA	25–800	10	–	0.2 l/min N_2	10 mg	FS 3.2, OS 1.0
		Fixed bed reactor	600	5	60 min	0.025 l/min N_2	100 g	
Polyethylene (LDPE and HDPE) and polypropylene [93]	Tarfaya (Morocco)	Autoclave	25–500 400, 450, 500, 525, 550, 600	2–10, 20	15 min	N_2	–	0.1
Shale oil sludge [97] a scanning electron microscope (SEM	Longkou (China)	TGA	50–900	10, 30, 50	–	0.05 l/min N_2	20 mg	0.2

"_" data not available

polyethylene HDPE, polypropylene) with high oil conversion and low char production led to co-pyrolysis products with a considerably higher yield of oil compared to that of OS. The quality and composition of the products were also noticed to change; for instance, the co-pyrolysis of LDPE improved the fuel properties of oil, somewhat decreased the content of sulfur and significantly decreased that of oxygen and polar compounds [92]. The co-pyrolysis oil obtained in this study was also reported to have a higher content of carbon and aliphatic hydrocarbons fractions, as well as improved fuel properties. Similar developments were also observed by Tiikma et al. [91]. The yields of liquids, gases and solids obtained from co-pyrolysis of OS and various feedstocks in different studies are presented in Table 4.

Table 4. Yields of products from co-pyrolysis of oil shale and various feedstocks

Feedstock	Oil shale	Blend ratio FS:OS	Oil yield, %wt	Gas yield, %wt	Water yield, %wt	Solids yield, %wt
Low-density polyethylene [91]	Kukersite (Estonia)	1:0	86	13	–	0.5
		1:1	55	10	–	32.9
		0:1	16	11	–	72
Polyethylene (LDPE) [92]	Goynuk (Turkey)	1:0	79.0	20.8	–	0.2
		1:3	71.3	16.0	4.3	8.4
		1:1	53.3	27.8	2.0	16.9
		3:1	37.0	26.1	8.8	28.1
		0:1	23.7	31.7	6.5	38.1
Polyethylene (LDPE and HDPE) and polypropylene [93]	Tarfaya (Morocco)	1:0	89–92	7-11	–	0.3–0.7
		1:1	51–54	5–7	–	41–43
		0:1	7.6	4.8	–	87.6

”–” data not available

3. Pyrolysis operational parameters

Determining the operational parameters is crucial for thermochemical conversion processes independent of the type of FS or reactor used. For pyrolysis, the atmosphere (inert or reactive), reaction temperature, FS particle size and heating rate affect the yield and composition of liquid, gaseous and solid products, as well as the efficiency of the process. These parameters also af-

fect heat transfer, the temperature gradients between particles and between the particles' surface and core, and the residence time, among other factors. The effects of pyrolysis temperature [98–103], particle size [104–106] and heating rate [107–110] on the fast, intermediate and slow pyrolysis of BM have been widely studied in different types of reactors and for different BM species. There have also been carried out numerous studies on the effects of temperature, particle size and heating rate on pyrolysis [111–117].

3.1. Steam atmosphere

The retorting of OS for the production of shale oil and shale gas has been studied using inert gas atmospheres (nitrogen, argon, or helium) for different purposes, such as kinetic analysis and modeling, TGA, product yield and composition analysis, and studies on the effects of different operational parameters [118–124]. Research on the pyrolysis of OS in different gas atmospheres (steam, H_2, CO_2) is scarce, even though the presence of steam as a gas atmosphere can potentially provide free hydrogen radicals, which can promote the decomposition of OS and increase the yield of shale oil [125].

Steam has been used with BM for different processes, such as liquefaction, torrefaction and carbon activation, and for improving the fuel properties of BM [126]. However, BM pyrolysis has been mostly studied in inert gas atmospheres, with only a few studies using gases such as steam, H_2, CO_2 and CH_4. Pyrolysis under steam atmosphere has been used to produce activated carbon, chemicals, liquid fuels [127, 128], hydrogen from bio-oil [129–131], and synthesis gas. The use of steam in pyrolysis has been proven to increase the yield of bio-oil and improve its quality, as well as the adsorption characteristics of activated carbons [132, 133]. Steam atmospheres influence the yields of products, especially liquid products [134, 135], owing to the efficient penetration of steam into the solids particles, which enhances the decomposition and removal of volatiles [136]. Steam works as a heat carrier, potentially reducing the need for external heating during pyrolysis [137]. Pyrolysis under steam atmospheres needs to be further studied as most of the research has been conducted only in fixed-bed reactors and has resulted in a limited production of liquid products on a commercial scale [34, 138]. Table 5 provides an overview of the studies on the pyrolysis of OS and BM using steam atmospheres.

The quality and composition of the products are improved in steam atmospheres compared to those in inert atmospheres. Different studies on the pyrolysis of OS under steam atmospheres demonstrated an increase in oil yield and weight loss (less solid residues) differently from N_2 atmospheres [125, 139, 140]. Steam was observed to affect the decomposition of OS positively, promoting the evaporation of oils from the shale particles, increasing the organic matter conversion, lowering the retorting temperature and minimizing the retrogressive reactions which lead to char formation. Higher steam flow

rates also promoted shale oil yield. Razvigorova et al. [125] noticed that in steam environments, the produced shale oil had a higher H/C ratio, higher fractions of neutral oil and heteroatomic compounds, light hydrocarbons, aliphatic compounds, asphaltenes and lower polar compounds. While studying the influence of steam on OS pyrolysis, Nazzal and Williams [140] noted steam to increase the contents of H_2, CO, CO_2, hydrocarbons, alkanes and alkene gases in the producer gas. El Harfi et al. [139] observed that not only the content of solid residue, but also that of sulfur in the semicoke decreased in steam atmospheres. However, the effect of steam atmosphere on OS pyrolysis needs to be further studied.

In the pyrolysis of BM, steam atmospheres decreased the yield of solid products and increased that of oil and gas unlike N_2 and static pyrolyses, as found by Özbay et al. [144] while comparing different atmospheric conditions. The pyrolysis of bamboo powder and woody BM in steam was studied by Kantarelis [141] and Kantarelis et al. [142] who noted divergences in the decomposition mechanisms, a faster decomposition rate, inhibition of the adsorption of tar vapors on char surfaces, and prevention of secondary tar cracking. Steam pyrolysis also contributed to the removal of low-molecular-weight compounds, thus reducing pore-clogging. The effects of steam were observed by Duman and Yanik [29] and Giudicianni et al. [136] to change with reaction temperature. High temperatures (> 500 °C) favor gas production and inhibit that of solids. Steam:BM ratios can also affect product yields. Kantarelis et al. [143] established that intermediate steam ratios promoted oil production, whereas high steam ratios inhibited oil yield.

The composition of BM and interactions between its components under steam atmospheres can affect the pyrolysis behavior, as observed from the individual and blended pyrolysis of lignin, hemicellulose and cellulose [136]. Lignin afforded the highest yield of char, cellulose the highest yield of liquid and hemicellulose the highest yield of gas, while in blends, the cellulose-lignin interactions strongly increased the yield of liquid and reduced that of char. The composition of the products can also change under steam atmosphere. Bio-oil can have a lower content of oxygen, a lower O/C ratio and a lower fraction of polar compounds, as well as a higher H/C ratio and higher fractions of aliphatic compounds and alkanes. Some researchers have found that the producer gas can generate higher yields of H_2 and CO_2 (due to the water-gas shift reaction), as well as of CH_4 and CO gas species, and give a higher high heating value (HHV) [143]. Moreover, the gas from steam pyrolysis increases the yields of H_2, CH_4 and CO, and also HHV, as it is not diluted with N_2 [142].

Overall, for BM and OS, steam atmospheres can act as reactive agents, hydrogen donors and heat and volatile carriers as they penetrate the solids particles and contribute to the desorption and removal of volatiles [144]. These atmospheres can produce positive effects during pyrolysis on the decomposition rate, heat transfer and heating rate, and trigger the prevention of secondary tar cracking and adsorption of tar by char particles.

Table 5. Experimental parameters of pyrolysis of oil shale and biomass in steam atmospheres

Feedstock	Experiment type	Temperature range, °C	Heating rate, °C/min	Residence time	Atmosphere	Sample mass	Particle size, mm
Tarfaya OS (Morocco) [139]	Fischer assay	550	10	20 min	150 cm³/min N_2 or steam	20 g	1.00–1.25
Krasava OS (Bulgaria) [125]	Hydrothermal treatment	400	30	25–30 min	steam	25 g	< 0.2
Sultani OS (Jordan) [140]	Fluidized-bed reactor	400, 450, 520, 570, and 650	–	45 min	N_2 or steam	–	1.20–3.33
Bamboo powder [141, 142]	Fixed-bed reactor	525, 875	–	9–12 min	1 Nm³/h N_2, 7.85 g/min steam	–	0.2–0.5
Pine and spruce [141,143]	Bubbling fluidized-bed reactor	500	–	300 min	20.8 l/min N_2, 0.5–1.0 kg/h steam	1.5–2.65 kg/h	1–1.4
Cellulose, hemicellulose, and lignin[136]	TGA	30–600	5	–	0.02 l/min N_2	1.5 mg	–
	Chamber test reactor	200–700	5–40	1.5–3 s	steam	6 g	–
Apricot pulp [144]	Fixed-bed reactor	550	5	–	100 cm³/min N_2, 2 cm³/min steam	10 g	–
Apricot pulp [145]	Fixed-bed reactor	300, 400, 450, 500, 550	5	30 min	2.5 cm³/min steam	10 g	~1.122

Table 5 (continued)

Feedstock	Experiment type	Temperature range, °C	Heating rate, °C/min	Residence time	Atmosphere	Sample mass	Particle size, mm
Pine, abies, maple and peach stones [146]	Box furnace	100–1000	–	30 min	0.02 l/min steam	250	Crushed
Cellulose, hemicellulose, lignin and Sugi (Japanese cedar) [134]	Superheated steam pyrolysis reactor	700	5–10	120 min	9 l/h water evaporated to steam	20–50 g	2.5 x 2.5 x 2.5, 0.01–0.10
Olive pomace [29]	Semi-batch reactor	500, 700	5	60 min	0.03 l/min N_2, 0.002 l/min steam	50 g	0.1–0.6

"–" data not available

3.2. CO_2 atmosphere

There have been carried out studies on reducing, capturing and utilizing the CO_2 produced from industrial, agricultural and domestic human activities, considering the detrimental effects of its emissions on the atmosphere [2, 147]. Pyrolysis of BM and OS using CO_2 atmospheres is an alternative to produce liquid bio-oil in enhanced atmospheres. CO_2 can influence the yield and quality of products [148, 149] and affect the behavior of FS during thermochemical conversion in terms of devolatilization and reforming of char and ash [150, 151]. In the pyrolysis of OS, CO_2 atmospheres can improve the properties of the products, such as the H_2/CO ratio in the producer gas [152]. There is not much research on the pyrolysis of OS using CO_2 atmospheres. Meanwhile, BM conversion in CO_2 environments has been studied, especially in BM gasification, where CO_2 can improve thermal efficiency, enhance tar cracking and promote dehydrogenation [149, 153]. CO_2 atmospheres have been observed to enhance the thermal efficiency of the process, unlike inert gas atmospheres [154, 155], while also increasing the CO production during fast pyrolysis [156] and decreasing the char production and CO_2 yield [157]. Table 6 lists experimental parameters used in various studies on the pyrolysis of OS and BM in CO_2 atmospheres.

The conversion of OS under CO_2 in pyrolysis or gasification processes has rarely been studied. Tang et al. [162] used CO_2 atmospheres for the pyrolysis of different types of Chinese OS. It was observed that the activation energy decreased in CO_2 atmospheres, contrary to N_2 atmospheres, and that the interactions between OS minerals, organic matter and CO_2 atmosphere resulted in a positive synergetic effect. Xie et al. [158] pyrolyzed Huadian OS in a CO_2 atmosphere, which resulted in a decrease of the solids yields. Differently from N_2, OS in CO_2 underwent further decomposition due to the gasification of carbon, which was transformed into CO. Moreover, CO_2 produced shale oil with large fractions of aliphatic hydrocarbons and long-chain hydrocarbons (C_{16}–C_{23}). The CO_2 atmosphere can promote interactions between the organic and mineral components present in OS as well as between the two former and the atmosphere itself.

Compared to N_2 pyrolysis, CO_2 pyrolysis of BM can yield higher quantities of non-condensable gases and lower quantities of solids and oils, as shown by Zhang et al. [157] in the pyrolysis of corncob, and by Ye et al. [159] in the pyrolysis of sawdust. The yield of gases increased in most of the studies carried out with different types of BM owing to the contribution of CO_2 in char gasification reactions, such as methane reforming, reverse water-gas shift and char gasification, which can enhance the thermal cracking of volatile organic compounds and favor reactions involving CO_2 and volatile organic compounds [156, 160]. Other benefits are observed in lower yields of CO_2 and higher yields of CO and H_2 owing to the cracking and reforming of oil under a CO_2 atmosphere. The bio-oil obtained has a higher HHV and a higher stability

Table 6. Experimental parameters of pyrolysis of biomass and oil shale in CO_2 atmospheres

Feedstock	Experiment type	Temperature range, °C	Heating rate, °C/min	Residence time	Atmosphere	Sample mass	Particle size, mm
Huadian OS (China) [158]	TGA	30–1200	20	–	0.08 l/min N_2 or CO_2	5 mg	< 0.28
	Fixed-bed reactor	30–500	10–20	–	0.1 l/min N_2 or CO_2	20 g	5–10
Corncob [157]	Fluidized-bed reactor	550	–	10 min	N_2, CO_2, CO, CH_4, and H_2	6 g	1–2
Pine sawdust [159]	Fixed-bed reactor	600, 800	–	15 min	0-80 vol% CO_2	1 g	< 2
Woodchips [156]	M-TG				100 vol% N_2, 20 vol% CO_2 and 80 vol% N_2	0.5 g	4–5
	Horizontal tubular reactor	850	–	–			
Sawdust and pinewood [160]	Drop tube furnace	900, 1100, 1300, 1450	–	500–600 ms	1 l/min N_2 or CO_2	5–10 g/h	0.125–0.250
Coffee, corn, oak, seaweed and *C. vulgaris* [161] oak wood, corn stover, macroalgae, microalgae, cellulose, hemicellulose, and lignin	TGA	25–800	20–400	–	0.06 l/min N_2 or CO_2	10 mg	< 2

"–" data not available

with large fractions of monoaromatic substances, polycyclic aromatics and phenols for the liquid products. For solids, the residual chars can have a higher porosity and a different morphology, increasing the access of reactants into the particles and promoting OS decomposition [160, 161].

3.3. Effect of temperature, heating rate and particle size on OS pyrolysis

The OS retorting process requires controlling different parameters to maximize the yield and quality of shale oil and shale gas and minimize residues. The pyrolysis reaction temperature, OS particle size and heating rate are among the most critical operational parameters that determine the quality, yield and efficiency of the retorting process [163–165]. Optimizing the pyrolysis parameters has contributed to reducing the amount of energy required for the retorting process and producing higher yields of products, especially shale oil [113]. The product yield is significantly affected by the heat transfer and heating conditions during the process. Some studies have focused on optimizing the shale oil production during OS pyrolysis [166, 167]. The effects of the pyrolysis reaction temperature, particle size and heating rate have been mostly studied through TGA and kinetic analysis [168–170]. Other studies have focused on the pyrolysis kinetics and reaction mechanisms of OS under different operational conditions [171–173]. The experimental parameters used in the studies of their effect on OS pyrolysis are listed in Table 7.

3.3.1. Temperature

Temperature has a significant effect on the product yield and residence time during pyrolysis (shorter residence time at higher temperatures). The yield of shale oil has been studied by Jaber et al. [177] and Olukcu et al. [178] at different temperatures in the 500–700 °C range. This temperature range has been used in numerous studies of the OS conversion process [39, 79, 80, 113, 164, 175, 176]. Several studies have found that temperature affects the yield of OS, resulting in a maximum yield in the range of 450–550 °C, with 520–525 °C being optimal for producing the highest shale oil yield [79, 93, 111, 113, 140, 174]. At temperatures over 550 °C, the pyrolysis process favors the gas yield owing to the secondary cracking or shale oil [81, 82, 140, 174]. Higher temperatures (above 550 °C) produce lower yields of semicoke and shale oil because of the catalytic effect of K, Na, Ca and Fe present in OS, which act as catalysts in the presence of steam, promoting the gasification of OS [85, 111]. Shale oil composition has also been observed to change with pyrolysis temperature. Higher temperatures (up to 525 °C) can produce oil with fewer fractions of asphaltenes and higher fractions of alkanes and aromatics, while decreasing the H/C ratio of shale oil [174].

Table 7. The effect of particle size, heating rate and pyrolysis temperature on the pyrolysis of oil shale

Oil shale	Experiment type	Temperature range, °C	Heating rate, °C/min	Residence time	Atmosphere	Sample mass	Particle size, mm
Huadian (China) [113]	Retorting system	25–430, 460, 490, and 520	3.67–9.57	40 min	–	50 g	0.0–3.0, 0.0–1.2, 0.0–0.6, 0.0–0.28
US Western OS [174]	Batch reactor	400, 450, 500	10	–	0.06 l/min N_2	200 g	–
Sultani (Jordan) [20]	Fluidized-bed reactor	520	–	45 min	Steam and N_2, 25–28 s residence time	0.75 kg/h (feeding rate)	0.20–0.60, 0.60–1.20, 1.20–3.33, 3.33–5.60
El-Lajjun (Jordan) [175]	Fixed-bed reactor	550	2–3	–	50 cm^3/min N_2	400 g	4–10
Huadian (China) [176]	Cylindrical retort	25–520	5, 8.5, 12, and 20	20 min	0.3 l/min argon	50 g	0–3
Tarfaya (Morocco) [111]	Fischer assay	400–600	12	–	0.15 l/min N_2 or steam	20 g	1.00–1.25
El-Lajjun (Jordan) [164]	Fixed-bed reactor	530	2, 5, 10, 15, 20, and 30	60 min	N_2 and steam (30 s residence time for steam)	–	1.20–3.33
El-Lajjun (Jordan) [115]	Fixed-bed reactor	340–600	0.2–2.8, 2.2–5.0, 7.0–13.0	–	N_2	500 g	0.5–2.1

"–" data not available

3.3.2. Particle size

The OS particle size affects several factors, such as the yield and composition of products, residence time, heat transfer and decomposition rate. The shale decomposition and the oil retained in the shale are inversely proportional to the particle size: large particles require longer residence times, resulting in higher yields of oil and non-hydrocarbon gases and lower yields of hydrocarbon gases. Moreover, the shale oil from OS of larger particle sizes has a higher content of carbon and hydrogen and a lower content of nitrogen, as well as higher quantities of aliphatic compound fractions and lower quantities of aromatic compound fractions due to the aromatization of oils, as observed by Nazzal [20]. However, a study by Khalil [175] shows how excessively large particles are affected by the heat diffusion from their surface to the core, leading to incomplete decomposition due to the slow heat transfer, requiring longer residence times and affecting the product yields. Meanwhile, small particles can provide a lower devolatilization of OS particle pores. The particle size is also dependent on the type of reactor; for example, fluidized-bed reactors require smaller particle sizes than fixed-bed reactors.

3.3.3. Heating rate

The heating rate in OS pyrolysis affects the product yields and can shift the main pyrolysis zone towards other temperature ranges. Different heating rates also affect the residence times, the penetration of thermal gradients towards the core of the particles and the decomposition of OS [37]. Wang et al. [176] observed a clear relationship between an increase in the heating rate from 5 to 12 °C/min and the final yield of shale oil. It was found that a heating rate above 12 °C/min resulted in a decrease in shale oil yield as higher heating rates impeded a sufficient sweep of the atmosphere gas to enhance the decomposition of OS. Another study, the one by Han et al. [113], found that an increase in heating rate up to 10 °C/min resulted in higher shale oil yields, which decreased when using heating rates higher than 10 °C/min, as it can result in the secondary cracking of shale oil. This observation was also confirmed by Nazzal [164] in the pyrolysis of Jordan OS where increasing the heating rate over 10 °C/min resulted in a slight decrease in oil yield.

The maximum yield of shale oil can be achieved at intermediate heating rates of 10–12 °C/min. Above these values, the shale oil yield decreases and the pyrolysis process enhances the yield of hydrocarbon and non-hydrocarbon gases due to secondary cracking and dehydrogenation reactions. Low heating rates require longer residence times for complete pyrolysis to take place. Lower heating rates can also lead to higher decomposition degrees as the particles are maintained at the same temperature for a longer time. Conversely, high heating rates may impede a complete pyrolysis process as the atmosphere gas does not have the required time to react with the OS particles and properly sweep the volatiles. At high heating rates, the oils cannot diffuse from the

OS pores, as found by Al-Ayed et al. [115]. At higher heating rates, the OS products are produced faster, thus being unable to diffuse out of the pores of the particles, leading to an increase in secondary tar cracking reactions and a decrease in product yields, especially shale oil's [164].

The shale oil composition is affected by the heating rate as high heating rates result in oil with a higher content of carbon, a lower content of hydrogen, and lower O/C and H/C ratios. High heating rates decrease the content of oxygen (more oxygen is transformed into non-condensable gases or char [176]) and sulfur in oil, producing lighter oil with a high content of asphaltenes, aromatics and benzene fractions. At higher heating rates, the content of the lighter fraction (light naphtha) in oil increased, resulting in a much lighter oil than crude oil. For the producer gas, as the heating rate increases, the contents of all the measured gases, including hydrocarbon and non-hydrocarbon gases, increase due to secondary cracking reactions [164, 176].

4. Conclusions

Co-pyrolysis of oil shale and biomass is a promising alternative for reducing environmental effects and improving the quality and yields of liquid and gaseous products. Co-pyrolysis using the currently available processing technologies is technologically and economically feasible, considering the similarities to the technology used in individual pyrolysis, as well as the economic, environmental and technical challenges of the individual pyrolysis of fuels. This study reviewed the different findings of recent co-pyrolysis studies, including the operational parameters, interactions, and yields and composition of co-pyrolysis products. The effects of the pyrolysis operational parameters on individual pyrolysis were also reviewed to serve as a guide for optimizing the co-pyrolysis of OS and BM.

The existence of interactions between OS and BM in co-pyrolysis is not definitive, as in some cases, the co-pyrolysis product yields prove synergy, while in other cases, co-pyrolysis behaves as an additive process of the pyrolysis of individual feedstocks. However, regardless of the existence of synergetic effects, co-pyrolysis of BM and OS results in products with improved quality and yield. These include a lower yield of solid products and a higher yield of oils with higher hydrogen and carbon contents and H/C ratios, and lower oxygen and sulfur contents. Co-pyrolysis triggers thermal decomposition and increases reaction temperature and activation energy. The main interactions in co-pyrolysis take place between FS ash, volatiles, inorganic elements present in FS and free hydrogen radicals (from BM), which promote the cracking of fuels. The improved co-pyrolysis products demonstrate the potential of using this process as a more sustainable alternative to producing valuable fuels and chemicals.

The effect of the operational parameters in the pyrolysis of OS and BM

proves that their optimization also plays an essential role in producing higher yields of improved products. Steam and CO_2 atmospheres speed up the decomposition of fuels, acting as reactive agents, heat carriers and volatile carriers and promoting the fuel cracking and interactions between the organic and mineral components. Temperature, particle size and heating rate strongly affect the decomposition and yields of OS and should be selected to ensure a complete decomposition of the fuel and release of all the volatiles.

The following suggestions would be beneficial for future research:

- While various studies have already been conducted based on themogravimetric analysis, the co-pyrolysis of BM and OS and the effect of operational parameters on a larger scale, using equipment such as prototype reactors and small-scale reactors, should be studied.
- The effects of reactive gases (CO_2 and H_2O) on the co-pyrolysis of OS and BM should be determined.
- The effects of catalysts on the co-pyrolysis of OS and BM should also be investigated.

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