

Co-Pyrolysis and Co-Gasification of Biomass and Oil Shale

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Abstract – The European Union has set an ambitious goal to transform to a carbon neutral economy. The present paper focuses on thermal treatment of oil shale and biomass blends that could be considered as an important pathway for achieving the carbon neutral goal locally in Estonia. The concept of co-pyrolysis and co-gasification of biomass and oil shale offers various advantages such as higher liquid product yield and higher char conversion than if the oil shale and biomass particles were processed individually. In the paper, an overview of the planned actions for merging oil shale industry carbon neutral economy is given. The selected approaches are justified with information found in scientific literature and initial experimental results. Further, the possible future developments for gasification and pyrolysis in Estonia are also highlighted.

Keywords – CFB (circulating fluidized bed); char; fixed bed reactor; heating rate.

1. INTRODUCTION

Biomass is an abundant raw material and a source for energy, fuels and (organic) chemicals. Producing fuels and chemicals allows more economical use of local biomass and waste. This is especially attractive for countries, like Estonia, that have large amounts of forested land.

Thermal treatment of different organic (polymeric) materials in an oxygen deprived environment, termed pyrolysis or gasification (depending on temperature), has received a lot of attention as a promising method to produce oil, chemicals and syngas. Studies have indicated that thermal treatment produces fuel (liquid or gas) at a lower cost than other common technologies, such as biochemical [1], [2]. Thermal treatment can be applied to a wide range of feedstock, including wastes and oil shale [3], which allows the use of different feedstock depending on what is economically feasible and readily available [4]. Such flexibility also means the raw materials could be varied to produce different types and amounts of products to meet changing demands. In addition, a locally important feedstock, such as oil shale could be used, either on its own or for co-pyrolysis/co-gasification with biomass to optimize the properties of the resulting liquid and/or gaseous product(s).

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Pyrolysis and gasification are complex processes involving hundreds of chemical species, many different reactions, and mass and heat transfer processes. The composition and structure of the raw materials and the conditions used all play a role in determining the composition of the evolving products [5], [6]. Performing co-pyrolysis/co-gasification, by mixing biomass with something like plastic wastes, tires or oil shale, also affects the process and the resulting products. On one hand, this can improve the yield and properties of the products and enable the use of a wider variety of feedstock, but it also adds complexity [7]–[9]. Further, compared to thermal treatment of just one raw material (for example coal), synergetic effects in co-pyrolysis and co-gasification are sometimes reported [10], [11]. It is also suggested that inorganic constituents can act as catalysts [6], [12].

The data on co-gasification of biomass and oil shale seems to be very scarce [13]. There are few studies on co-pyrolysis of oil shale and biomass at temperatures ranging from 340 °C in an autoclave [14] to 520 °C in a cylindrical retort [15].

The current paper presents a broad range of conditions and techniques that are used in the ongoing study intended to develop knowledge in the field of co-pyrolysis and co-gasification of oil shale and biomass. The results obtained provide valuable input to the analysis of the perspectives of Estonia's carbon neutrality and also to the oil shale industry for developing innovative and environmentally friendly technologies for oil shale processing. Firstly, it will provide basic information about the possibilities for further valorisation of feedstock for example into platform chemicals and polymer monomers. Secondly, valuable data is obtained to cope with the targets of the European Union climate and energy package and Renewable Energy Directive.

2. METHODS AND MATERIALS

2.1. Raw Material

The selected approaches are applied to Kukersite oil shale, biomass and their mixtures. Proximate and ultimate analysis of the biomass (bark of Scots pine; *Pinus sylvestris* as an example) and oil shale are shown in Table 1. To eliminate the effect of moisture content, samples are dried at 105 °C and stored in desiccators. Particle size of the sample is in between 0.25 mm and 0.5 mm.

TABLE 1. EXAMPLES OF PROXIMATE AND ULTIMATE ANALYSIS OF BARK AND OIL SHALE

	Loss on ignition at 550 °C, wt. %	Ash content at 815 °C (dry matter), wt. %	Carbonate CO ₂ , wt. %	Elemental composition, wt. %				
				C	H	N	S	O
Oil shale	41.38	47.35	17.6	33.78	3.71	0.09	1.73	60.69
Bark (Scots pine)	96.95			52.79	6.08	1.19	0.04	43.10

2.2. Testing Procedure

The general test plan is as follows:

- 1) Sample preparation – particle size-reduction;
- 2) Preliminary characterization of fuels – it involves elemental composition, content of heavy metals, calorific value, ash content, moisture content, adsorption parameters, etc.;

- 3) Thermal treatment of materials in thermogravimetric analyser (TGA) under different conditions (pyrolysis or gasification). Different heating rates and carrier gases can be used (usually below 40 °C/min) to test a wide range of conditions. As the sample amount is limited, it is mostly used for screening, although valuable data on evolving gases is obtained;
- 4) Thermal treatment of materials in a fixed bed reactor is used to obtain larger amounts of material that can be further analysed and characterized. For the solid residue (char), the same analyses are carried out as for preliminary characterization of fuels. Evolved gases and condensed oil are further characterized.

2.3. Experimental Set-Up and Equipment

The experimental part of the research is performed in the Department of Energy Technology (DET) of the Tallinn University of Technology. The co-pyrolysis and co-gasification experiments are being performed in a laboratory-scale fixed bed reactor (Fig. 1), described in more detail in [16]. It is equipped with control (temperature control by means of thermocouples and gas flow by means of mass flow controllers) and data acquisition system (NI SCXI-1000 chassis with modules NI-1102 and NI-1124). Non-condensable gases may be analysed either with Fourier transformed infrared (FTIR) spectrometer (*DX-4000, Gaset*) which can be configured to measure simultaneously H₂O, CO₂, CO, NO, NO₂, N₂O, SO₂, NH₃, CH₄, HCl, HF, C_xH_y. The FTIR is coupled with a Zirconia oxygen sensor for determination of the O₂ content. Concentration of volatile organic compounds (VOCs) is measured using a flame ionization detector (*Fidamat 6, Siemens*). Samples of the evolving gases may also be extracted to the gas sampling bag for the later analysis (of CO, H₂ and CH₄).

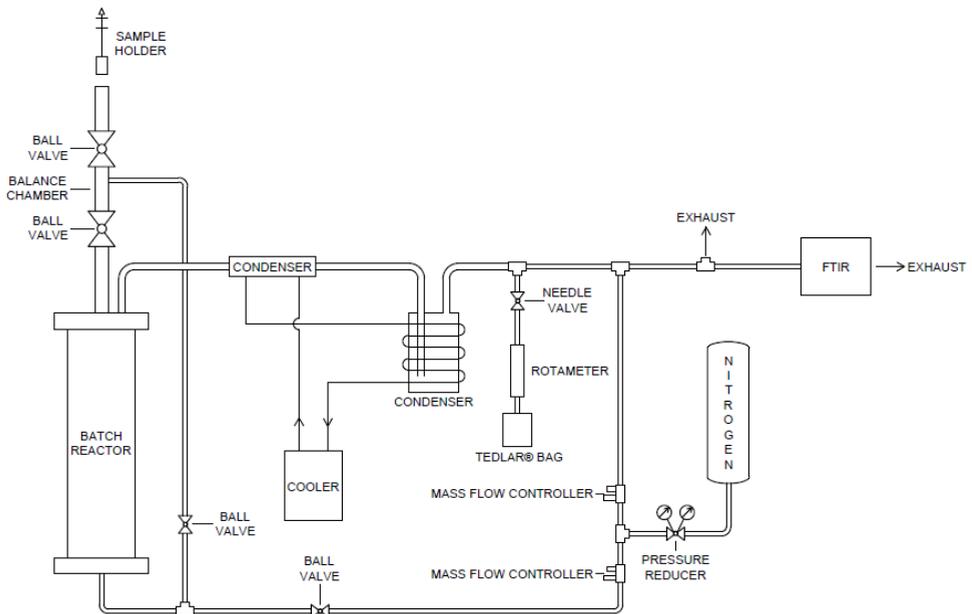


Fig. 1. Fixed bed reactor set-up.

The kinetics of the gasification and pyrolysis processes including also heat effects are measured with a *Netzsch STA 449 F3 Jupiter®* thermogravimetric analyser. It is equipped with a water vapor generator and high-speed furnace to simulate processes under different conditions and different heating rates. Evolved gases are analysed with *Netzsch QMS 403 D Aëolos®* mass spectrometer.

Determination of adsorption parameters (specific surface area and porosity, including calculation of multipoint BET, void volume and micropore specific surface area) is performed using a Quantachrome Autosorb iQ-C gas sorption analyser. It is useful for physisorption and chemisorption studies (former in H₂ and oxidizing environments) to fully characterize the feed materials and the remaining solid residues.

The mobility of heavy metals is analysed using ICP-MS (*Thermo iCAP Qc Quadrupole*) after acid digestion and treatment.

Gases and liquids will be analysed in gas chromatograph (*Agilent 7890A GC*) with MS and FID detectors and LC (*Waters e2695*) with PID and MS detector, respectively.

General sample characterisation (including chemical composition of solids) is performed in a dedicated accredited laboratory in DET according to international standards and validated methods.

3. RESULTS AND DISCUSSION

Despite the efforts taken to reduce the use of solid fossil fuels, combustion of these fuels is still one of the main sources of electricity and heat, both in Estonia and globally. This is mainly because these fossil fuels are widely available, and the technologies used are reliable and available when needed. Oil shale provides approximately 80 % of Estonia's electricity needs, making Estonia one of the least energy independent countries of Europe [17]. The oil shale sector is known from wider publicity about its large environmental footprint. However, it is not often known that, during the last 25 years, significant improvements in reducing the environmental impact of the oil shale-related industries (both energy and shale oil production) has been achieved. This is mainly as a result of utilizing fluidized bed combustion technologies. At the same time, new technologies are emerging that could possibly provide even more efficient utilization of oil shale and provide cleaner and more economical energy. To find the balance between the needs (energy) and expectations (clean environment), it is necessary to develop more sustainable ways to utilize local conventional fuels (such as oil shale). Also, latest developments in the energy sector are mostly driven by the EU's legislative constraints and climate agreements suggest that further development of the oil shale industry is urgently needed. It is suggested that instead of oil shale combustion, its gasification or valorisation to shale oil could be more sustainable [18].

Estonian oil shale pyrolysis process is rather well studied and shale oil is extensively researched [19]–[21]. In the pyrolysis reactors, the conditions have been optimized to maximize the yield of shale oil. Shale oil is mostly used as fuel oil and its value depends on the crude oil market. To increase the value of shale oil, it should be further processed using upgrading (for example with the aid of gas) or separation of valuable compounds to be used in the chemical industry. Dibasic phenols have been the main valuable products separated from the Kiviter shale oil (low heating rate). Recently a project for oil shale valorisation was started with the aim to use partial oxidation of kerogen for production of dicarboxylic acids [22], showing the potential of oil shale as a source of valuable products. However, little is known about the liquids obtained during its co-pyrolysis with biomass. Based on the coal and

biomass pyrolysis liquid characterization, it could be expected that, depending on the type of feedstock, the obtained products could be “modified” [23].

The composition and yield of the products obtained during their thermal treatment is dependent on the type/composition of the feedstock that is used in the process, process temperature, heating rate, reaction time and the feed particle size [24]–[26]. In the following sections, a short overview describing the effects of these different parameters on pyrolysis and gasification processes is given together with the parameters selected in the current study and their possible impact on the process and products.

3.1. Feedstock

Biomass (based on the species analysed as well as storage conditions) could have significant variation in its physical as well as chemical properties. The composition of oil shale, mainly its organic content, however, also chemical composition of organic matter, is also varying. The parameters of feedstock affecting its thermal treatment and composition of obtained products are the size of the particles, ratio of oil shale to biomass, ash content, moisture content (which determines the concentration of steam in the gas phase). The feedstock blending ratio is reported to directly affect the formation of combustible gases (mostly H₂, CO and CH₄ but also higher hydrocarbons) in co-gasification [27]. Additionally, biomass blending with coal is reported to initiate gasification process at lower temperatures [28], produces more tar and less char [27].

In the course of the research, we have chosen to keep the size of the feed particles small to reduce the diffusion related phenomena and to reduce the time needed to heat the particles. Also, to avoid adding complexity, the samples are always dried. Rather, moisture (in the form of vapour/steam) can be introduced into the reactor in a controlled manner. Steam is a commonly used “additive” in gasification of biomass or coal as it allows to effectively change the composition (for example H₂ or CO content) of obtained gas [29].

An important feature that distinguishes oil shale is its high mineral matter content. This mineral matter is largely composed of carbonate minerals that start to decompose at temperatures of around 700 °C (Fig. 2). During decomposition a significant amount of CO₂ is formed. The extent of carbonate decomposition depends on the final temperature and residence time [30].

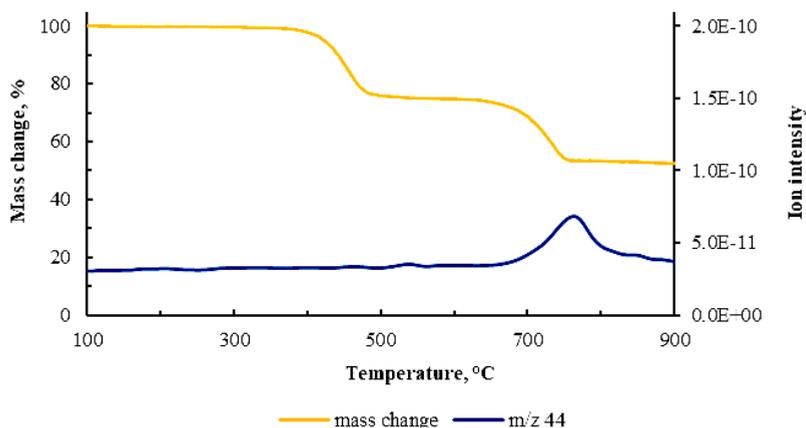


Fig. 2. Decomposition of oil shale and evolution of CO₂ in N₂ atmosphere.

As can be seen from Fig. 2, the sample displays mass loss steps typical for oil shale – the decomposition step for organic matter in the temperature range of 370 to 560 °C and the decomposition of carbonate minerals in the temperature range of 600 to 770 °C. These have respective mass losses of 24.7 % and 21.9 %. Additionally, about 0.5 % of moisture is present (mass loss up to 200 °C). The residual mass of the sample is 52.8 %. The blue line on Fig. 1 shows the evolution of m/z 44, CO_2 . As it is evolving at temperatures above 700 °C, it confirms that the second mass loss step is the decomposition of carbonate minerals while little or no CO_2 is evolving during decomposition of organic matter.

3.2. Temperature and Heating Rates

Temperature is quite influential as far as the results of the pyrolysis products are concerned. For example, during the pyrolysis of biomass (and other feedstock) the composition of evolving gases changes as temperature is changed as does the amount of char. It has been studied that at higher temperatures more non-condensable gases [31]–[33], mainly $\text{CO} + \text{H}_2$, are formed. In contrast, if the process is done with lower temperatures, solid products like charcoal, bio-coal or torrefied fuels are produced [23].

Together with temperature the heating rate also has a large influence on the yield and composition of the product that can be obtained in the processes. For example, if the material is heated rapidly to a moderate final temperature, more liquids will be obtained [34] whilst increasing the temperature and maintaining the high heating rate results in higher gas yields [35], [36].

In the current study, the main emphasis is on the gaseous and liquid products. Therefore, the sample is introduced to the pre-heated reactor (so-called drop-in method). In this way we achieve the highest possible heating rate to increase the yield of gases/liquids (depending on the final temperature). It is expected that the study will provide sufficient data for upgrading the process.

Low heating rate thermal treatment studies indicate that there is two-step decomposition (pyrolysis) taking place at temperatures below 500 °C (Fig. 3). At higher heating rate (in fixed bed reactor) the decomposition of oil shale and biomass seems to be simultaneous (Fig. 4).

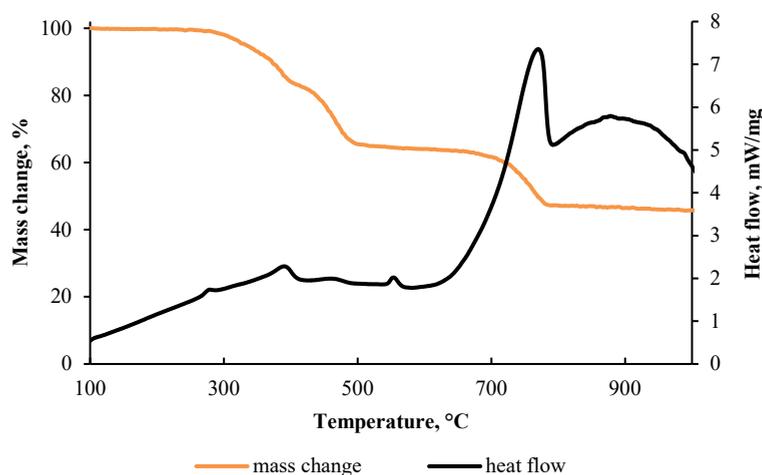


Fig. 3. Decomposition of oil shale and biomass mixture (80:20 w:w) in N_2 atmosphere.

In Fig. 3, the mass loss and heat flow during pyrolysis of oil shale and biomass mixture is shown. Compared to the oil shale decomposition presented in Fig. 2, the mass loss during co-pyrolysis starts at approximately 100 °C lower temperature (around 280 °C) which corresponds to the starting point of wood pyrolysis [37]. Heat effects associated with pyrolysis are rather small compared to that of decomposition of carbonate minerals.

Based on the decomposition data from TGA and gas analysis data (Fig. 4), the estimated heating rate (from 25 to 300 °C) of a sample in fixed bed reactor is around 140 °C/min.

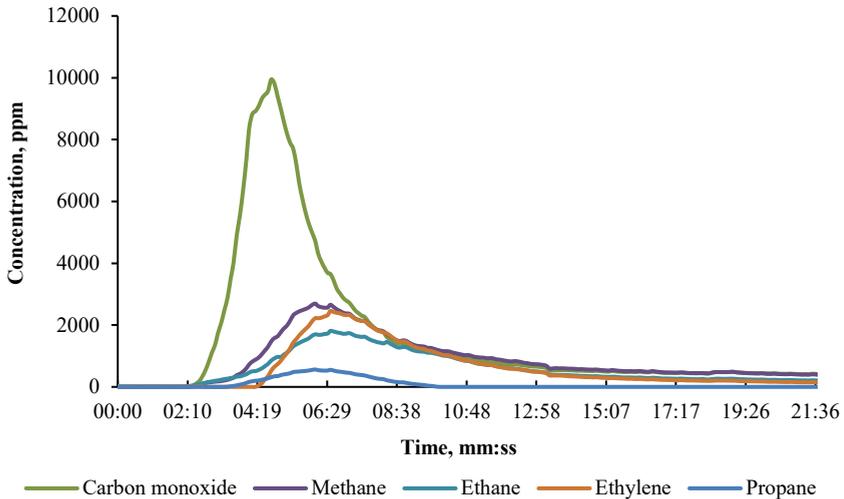


Fig. 4. Evolution of different gases during oil shale and biomass co-pyrolysis at 550 °C in the fixed bed reactor.

At high heating rates there is no possibility to measure real time mass loss, however, the process can be monitored through gas analysis. The gas analysis shows that at pyrolysis conditions relatively large amount of higher non-condensable (at around 0 °C) hydrocarbons is formed. Further studies are underway to determine the possible catalytic effect of oil shale on biomass co-pyrolysis (for oil production) and co-gasification (especially for production of syngas with high CO and H₂ content).

3.3. Reactors

There are different reactors available for co-pyrolysis or co-gasification. The selection of a reactor for the thermal treatment defines the occurrence of the reactions and exact processes involved in different reactor zones which are interrelated with temperature effects. There are different types of reactors used for pyrolysis and gasification. Fast pyrolysis reactors have been developed for the purposes of laboratories and pilot-scale demonstrations, including CFB, free fall etc. types [10]. Operational gasification (pilot) plants are gathered in the International Energy Agency (IEA) database [38]. For coal and biomass co-gasification, a total of five plants at least in the technology readiness level (TRL) 4–5 have been built. Plants utilizing down draft fixed bed gasifier and Integrated Gasification Combined Cycle (IGCC) have failed to reach commercial operation. Currently, according to IEA, only two pilot scale plants (pressurized entrained flow gasifier and fixed bed gasifier) in the Research Institutes of Sweden are operational. Regarding biomass and coal co-pyrolysis, two TRL 6–7 fast

pyrolysis plants in the world are operational, however, at least one pilot scale fast pyrolysis plant is also operational in the VTT technical research centre of Finland.

Despite the unfavourable statistic, the studies of pyrolysis and gasification are continuing. For this purpose, different reactors are utilized, including fixed bed, downdraft fixed bed, updraft fixed bed, (circulating) fluidized bed, tubular, entrained flow and circulating radial-flow moving bed reactors [10].

The reactor used in the current study is a batch fixed bed reactor which was chosen for its simplicity. As this type of reactor is used for developing new processes (or studying for example solid-supported catalysts), it serves as an excellent reactor type for oil shale and biomass blends gasification and pyrolysis.

3.4. Char

Char is sometimes considered as a leftover of pyrolysis or gasification processes, however, depending on its properties, bio-char can be used as fertilizer or soil improver [39], [40] or other value-added product (e.g. catalyst carrier). Compared to the use of conventional fertilizers, the addition of bio-char to the soil will reduce CO₂, CH₄ and N₂O emissions [41], [42]. Despite its beneficial properties, it is still advantageous to reduce the amount of char formation if the goal is to use fuels as a source of liquids or gaseous products [43], [44]. This will be achieved as temperature is increased as is shown in Table 2. As it can be seen for pyrolysis of biomass, the mass losses obtained in the fixed bed reactor are between 80–88 % which is commonly reported in literature [45]. Interpretation of oil shale thermal treatment results is more challenging because of the high content of carbonates in mineral part of oil shale.

The mass losses of co-pyrolysis calculated (based on Eq. (1)) from the obtained losses in pyrolysis of biomass and oil shale are 42.62 %, 45.54 % and 56.88 % at 550 °C, 750 °C and 900 °C, respectively. These values are higher than those obtained experimentally in co-pyrolysis, indicating possible synergy between the materials.

$$ML_{\text{theor}} = \frac{m_{\text{BM}} \cdot ML_{\text{BM}} + m_{\text{OS}} \cdot ML_{\text{OS}}}{m_{\text{SUM}}}, \quad (1)$$

where

ML_{theor}	Calculated mass loss at specific temperature, %;
ML_{BM}	Experimental mass loss of biomass at specific temperature, %;
ML_{OS}	Experimental mass loss of oil shale at specific temperature, %;
m_{BM}	Mass of biomass, g;
m_{OS}	Mass of oil shale, g;
m_{SUM}	Mass of oil shale and biomass blend, g.

Still, as the easiest option, char can also be beneficially used to extract energy from residual carbon. Estonia has extensive experience in utilizing char (called semi-coke) as an energy source in solid heat carrier shale oil production processes (so-called Galoter process including Petroter and Enefit technologies) [46].

Oil shale pyrolysis residue, semi-coke (or char), is known by its environmental hazard [47]. Still, considering different beneficial options for char utilization, solid residues from co-pyrolysis and co-gasification experiments needs to be fully characterized.

TABLE 2. MASS LOSSES DURING THERMAL TREATMENT OF OIL SHALE, BIOMASS AND THEIR BLENDS

Sample	Temperature, °C	Mass loss, wt.%
Bark (Scots pine)	550	80.60
	750	85.45
	900	87.62
Oil shale	550	24.54
	750	26.54
	900	42.24
Oil shale + bark	550	39.56
	750	46.67
	900	60.46

3.5. (Co-)Gasification: Current Situation and Future Directions

Gasification is considered an economically efficient process when it comes to utilization of low-grade fuels [48], [49]. Gasification of oil shale was historically carried out in chamber ovens and resulted gas which had medium calorific value and relatively high sulphur content. High sulphur content of chamber oven gas made it unusable (according to the current standards) in most applications. When combining the accumulated knowledge with modern gasification processes, it might be possible to reconsider oil shale gasification, and more preferably co-gasification with biomass, as an economically and environmentally viable process. This could be achieved with CFB gasifiers that have a high fuel flexibility. Based on the experience and current trends in combustion related studies, as well as trends in pyrolysis and gasification studies, it is generally accepted that CFB technology is the preferred technology. This technology is well suited for high ash content fuels like oil shale and allows more simple and precise control of gasification environment and temperature control compared to other, more conventional gasification technologies. CFB technology also ensures uniform temperature distribution which is an important parameter considering the effect of temperature on gasification products. Currently, however, there is no information available on gasification of oil shale in CFB reactors. The current study is intended to provide data on the CFB gasification conditions and resulting gas composition (including tar formation) useful for scientists and decision makers. Consequently, the results of the study will be used to upgrade gasification to a CFB unit that is currently under development in DET.

An important goal in future studies is to evaluate the possibility of utilization of CFB gasification technologies for oil shale and biomass co-gasification that could easily be adopted on a large scale. It is important to comprehensively tackle the currently known problems, like de-fluidization of the fluidized bed caused by the agglomeration of biomass ash with low melting point and excessive tar formation and accumulation in downstream pipes [50] that have resulted in failure of pilot and large-scale installations.

Additional studies should also focus on environmental aspects of provided processes. This includes greenhouse gas and sulphur emission related problems. Because sulphur is a dangerous pollutant (for the environment and for catalyst if obtained gases are further used in synthesis), its removal from streams is of high importance. Therefore, the fate and behaviour of sulphur compounds should be studied to determine the operational conditions for maximizing the extent of sulphur bound to the mineral part of oil shale in co-pyrolysis

and co-gasification processes. Most importantly, it must be ensured that all environmental aspects of the proposed technologies are considered so that the stakeholders and the wider public accept the technologies.

3.6. (Co-)Pyrolysis: Current Situation and Future Directions

Estonian oil shale chemical industry is relying on an old, out-dated Kiviter process. This process is known by its large environmental footprint and issues with pyrolytic water [51], however it produces oil with higher content of methylresorcinols. On the other hand, it is known that biomass pyrolysis oils have a complex chemical composition and they contain many useful oxygen and nitrogen compounds that can be used for producing chemicals [2]. Therefore, biomass and oil shale co-pyrolysis oil could potentially contain different valuable compounds that would help to extend the chemical industry and make it environmentally acceptable.

After completing this study, an immediate direction for further research would be to develop applications in detail for the most valuable chemicals found in the co-pyrolysis oils. Certainly, some basic platform chemicals and polymer monomers can be produced [2], but beyond this there are a lot of high-tech applications that should be investigated. For example, the phenolic compounds can be used to create carbon aerogels, which can then be used in capacitors and batteries, insulation, adsorption and filtration and other applications [52]–[54]. Such phenols are also valuable precursors of adhesive resins for certain plastics. There is large potential to investigate other high value applications of chemicals from co-pyrolysis liquids.

4. CONCLUSIONS

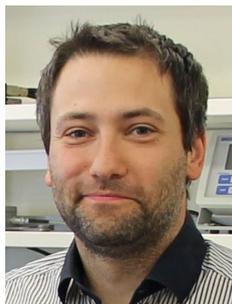
Co-pyrolysis and/or co-gasification of oil shale and biomass seem to be a feasible intermittent step for achieving the final goal of transforming Estonia to a carbon neutral economy and is meaningful in regards to circular economy goals (effective use of wood waste for co-pyrolysis and co-gasification). However, as this conclusion is based on the literature reviews on thermal treatment of coal and biomass blends, further oil shale specific experimental data is needed. An important feature distinguishing oil shale from most of the coals is its high mineral matter content which means careful selection of process parameters is needed. Experiments do show that heating rate has a strong effect on the process and the main focus should be on thermal treatment of blends at high heating rates. Not only yield of products, but also environmental aspects need to be considered. To take full advantage of the feedstock, all process streams must be researched.

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