TALLINN UNIVERSITY OF TECHNOLOGY
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Department of Materials and Environmental Technology

THERMAL ANALYSIS AND MODELING STUDIES OF BLENDED FUELS IN OXY-FUEL COMBUSTION

KÜTUSESEGUDE HAPNIKUSPÕLETAMISE TERMOANALÜÜS JA MODELLEERIMINE

MASTER THESIS

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AUTHOR’S DECLARATION

Hereby I declare, that I have written this thesis independently.
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Tallinn, May 15th, 2017

Serkan Sener

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List of Abbreviations

CCS	Carbon dioxide capture and storage
CFB	Circulating fluidized bed
DTA	Differential thermal analysis (heat effects)
DTG	Differential/derivative thermogravimetry
EOS	Estonian oil shale
FGR	Flue gas recycle
GHG	Greenhouse gas
HHV	Higher heating value
IGCC	Integrated gasification combined cycle
OF	Oxy-fuel
OS	Oil shale
PC	Pulverized combustion
PSD	Pine sawdust
SC	Semi-coke
SCE	Semi-coke Estonia
TA	Thermal analysis
TG	Thermogravimetry
WC	Wood chips
WP	Wood pellets

1. INTRODUCTION

1.1. General Outlook

Energy and the environment are the two most significant issues in this century as the demand for energy has been increased rapidly due to rise in world population and economic growth. If the energy resources are used in the same way, the societies will face with serious environmental problems and eventually ecosystem collapse will be an inevitable result in near future. Thus, different approaches which can avoid serious disasters are necessary for a sustainable development.

Currently, 85% of the energy supply of the world relies on fossil carbon such as coal, oil shale (OS), peat, liquid oil and gaseous natural gas. These fuels are non-renewable and they are consumed about a million times quicker than they are formed. As a result, CO_2 emission is increasing and the limits which have been set by planet are about to be achieved as early signals have already been taken as global warming and climate change. Greenhouse gas (GHG) emissions are recognized as the major contributor to global warming and have a long-term influence on climate change. The fourth report of *Intergovernmental Panel on Climate Change* states that the significant increases of GHGs in the atmosphere through post-industrial period are a result of human activities mainly due to the burning of fossil fuels and various chemical processes [1].

Furthermore, the *World Energy Outlook* projects propose that the world's population is foreseen to rise by around 1.5 billion till 2035. Depending on this population rise and growth in the world economy, more energy is required and energy consumption is anticipated to increase by 34% until 2035. *Figure 1* illustrates the expectations on worldwide energy consumption by fuel source. It can be seen that fossil fuels will remain as dominant source by accounting for almost 80% of total energy consumption in 2035 [2, 3].

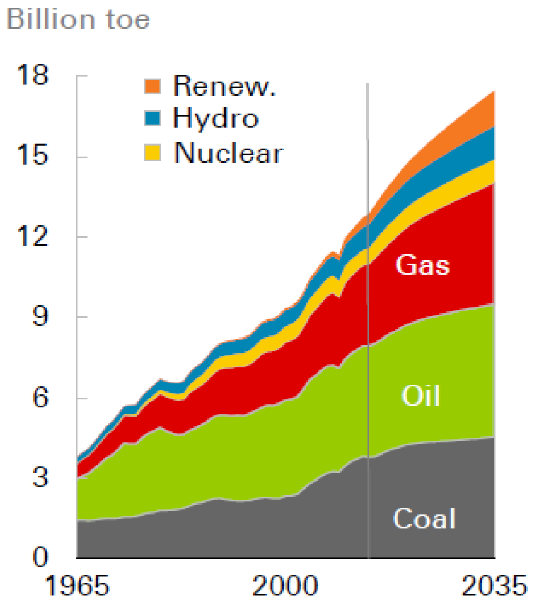

Figure 1. Energy consumption by fuel source [3].

If this scenario becomes true, the usage of fossil fuels on a massive scale will lead to the accumulation of CO_2 emissions in the atmosphere and we will experience even higher temperatures and bigger risk of global warming in the near future. Thus, the abatement of CO_2 emissions and mitigation of the negative consequences are now an urgent challenge in order to solve the increasing problem of climate change.

The reduction of CO_2 emissions from fossil fuel-fired power generation can be accomplished by various technologies and new methods. The expansion of renewable energy as an important solution will be high on the agenda, especially in Europe, and there will be tendency to decline the share of non-renewable resources in primary energy generation as additional primary energy will be more and more supplied from renewable sources which will have direct impact on CO_2 emissions. However, according to today´s global energy policies and projections, the immediate energy demand of the world is still likely to be supplied by the fossil fuel combustion until respective renewable energy sources can be sufficient to produce significant amount of energy. In this transition period, new pathways and technologies should enable the continuous usage of fossil fuels, however, at the same time they should eliminate the emission of CO_2 [4, 5]. In this context, CO_2 capture and storage (CCS) appears as a key aspect and provides a step change reduction in CO_2 emissions which are generated from fossil fuel combustion and in these ways fossil fuels can continue to be used efficiently and in a sustainable way. *Figure 2* shows the possible technologies for reducing CO_2 emission that are proposed in the report of *International Energy Agency (IEA) Projection 2050*.

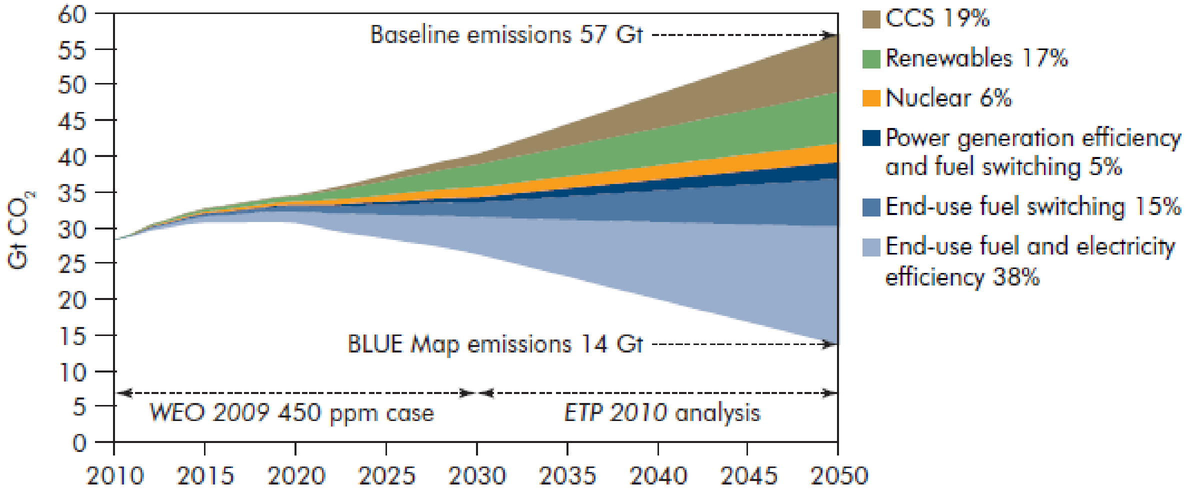

Figure 2. Key technologies for reducing CO_2 emissions [6].

According to this report, the development and deployment of a wide range of energy efficient and low carbon technologies across every sector of the economy are required for achieving the desired CO_2 emission reduction. Among these technologies, CCS technology has 19% potential to decline CO_2 level as one of the important elements in the respective strategy [6]. CCS consists of three main technologies: pre-combustion, post-combustion and oxy-fuel (OF) combustion. Additionally, chemical looping is yet another CO_2 capture technology which has also increasingly been studied in CCS [7]. *Figure 3* shows the main operations related to the post-combustion, pre-combustion and OF combustion technologies [4].

The OF combustion is one of the technologies in CCS and it is widely known from the experiences of coal and biomass firing in pulverized combustion (PC) and circulating fluidized bed (CFB) boilers. The successes of theoretical examination of OF combustion and accumulated bench and pilot-scale tests have led to several industrial-scale demonstrations since 2008 [8, 9, 10]. This progress is mainly due to the perceived superiority of the technology as it is viewed as a simple, but effective. For example; unlike post-combustion capture, there is no need to add a complicated chemical process to capture CO_2 and there is also no need for the power generation industry to adopt a completely new process such as integrated gasification combined cycle (IGCC) as in the method of pre-combustion process.

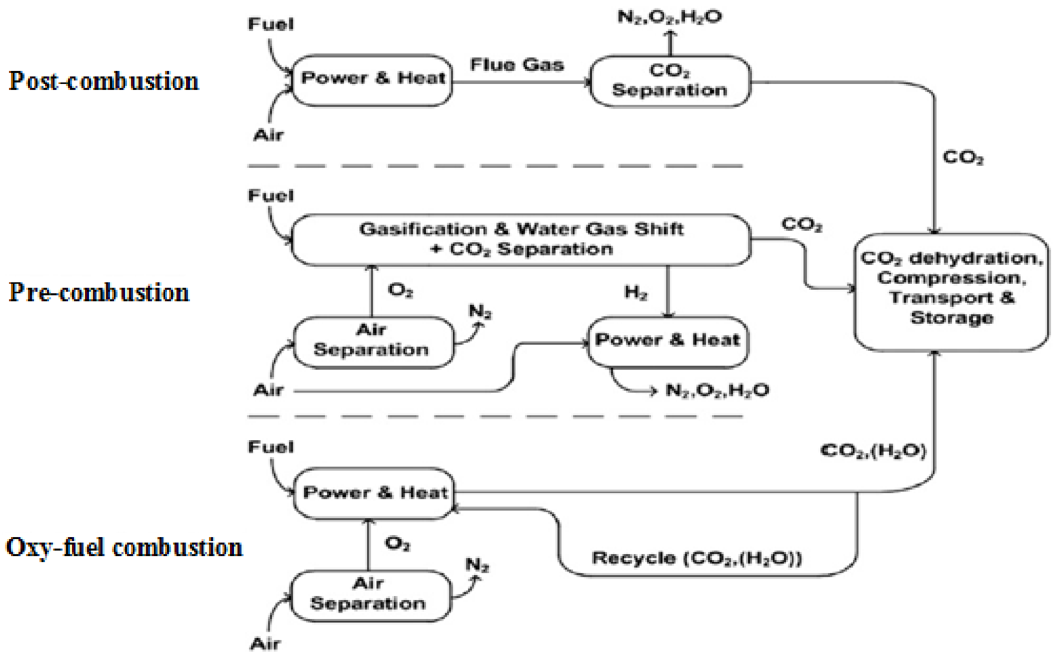

Figure 3. Three main categories of carbon capture technologies [4]**.**

Today, OF combustion technology is at a point where it is considered near commercial from a technological point of view and several steps are now being undertaken for the successful large-scale demonstration plant in several countries such as U.S., UK, and China [11-13]. By further improving the economics of the OF combustion, it is likely that OF combustion will be key player to overcome the problem of CO_2 emissions especially originated by the combustion of solid fuels such as coal, OS, peat etc.

1.2. What is best for Estonia?

Estonia is largely self-sufficient in terms of energy and is able to meet its electricity and heat needs from a domestic source–namely OS. Today, OS is used directly in both PC and CFB boilers and also for producing shale oil via retorting process. Especially the conventional combustion of OS provides a relatively high degree of energy security in Estonia. However, excessive usage of OS leads to a high carbon footprint, problem of storing its ash thus raises the questions of long-term sustainability. Besides, in the case of thermal processing of one ton of dry OS, 130-160 kg of shale oil and 450 m^3 of retort gas are obtained and up to 600 kg of a harmful solid waste such as semi-coke (SC) are formed [14]. Almost 110 million tonnes of SC have been deposited at retorting plants since 1921 when OS retorting started in Estonia [15]. Today, large amount of SC continues to be formed from Estonian OS power industry and it is difficult to store such a large amount hazardous SC in piles. Furthermore, residual organics in SC and leachates of it contain phenols, polycyclic aromatic hydrocarbons (PAHs) as well as oil products that are potential pollutants with harmful environmental effects. Thus, finding a possible solution for the utilization of SC is very important in order to avoid its harmful effects for the nature and underground water [15].

Based on the operation experiences of direct firing of Estonia OS (EOS) since 2004, CFB boilers appear for the time being to be more suitable for low-rank, high-sulfur and high ash fuels like EOS in terms of combustion efficiency and reduced emissions including CO_2. However, due to the massive usage of EOS in heat and electricity production, the reduction in CO_2 emission is still a great challenge. There have been complex and significant environmental policy issues and challenging consequences due to the CO_2 emissions and wastes from OS combustion in Estonia. Estonia, as a member of European Union (EU), will continue to face similar issues according to the long-term goals set by EU to reduce greenhouse gas emissions by 80-90 % till 2050 compared to the emission values in 1990, if appropriate steps are not taken in the near future [16, 17].

As a part of achievement process, relevant steps have to be taken, and Estonia has to focus on low-carbon transition considering its technological and economical potential. For this reason, OF combustion technology with CCS can be a great option and the usage of alternative renewable energy source such as biomass in power production could give a degree of flexibility to Estonia’s OS capacity. In this respect, implication of modern technology by increasing the share of biomass in energy production and also by focusing on the utilization of solid wastes from OS retorting including its residual energy potential for combustion with partial fuel switching from 100% OS to OS co-combustion with biomass and SC can be a good option and these applications can also be brought up to date with the CFB–OF combustion technology for more sustainable and environmentally friendly usage of OS.

2. LITERATURE REVIEW

2.1. Oxy-fuel combustion

OF combustion technology was firstly proposed by Abraham et al. to produce large amount of CO_2 for enhanced oil recovery in the early eighties. However, recent developments have led to a renewed interest in the technology regarding the reduction of environmental impacts caused by burning of fossil fuels for energy generation [4]. Today, OF combustion technology is suggested as one of the promising technologies considered for capturing CO_2 from power plants with CCS. The concept of the OF combustion involves the removal of nitrogen from the air and burning the fuel with a mixture of nearly pure oxygen (typically higher than 95% purity) and recycling the flue gas. *Figure 4* illustrates the OF combustion process.

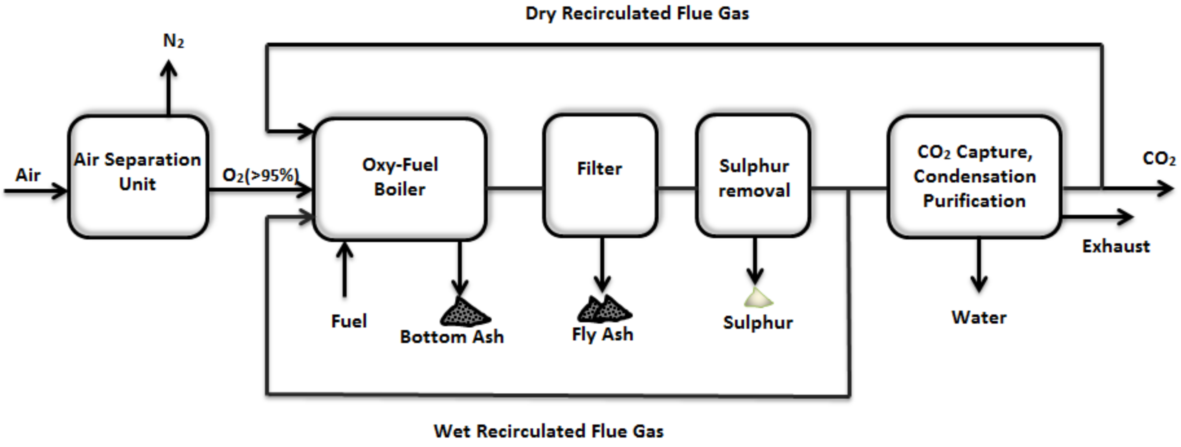

Figure 4: OF combustion process.

Flue gas recycle (FGR) is used to control the flame temperature and create volume of the missing N_2 to achieve the temperature and heat flux profiles in the boiler similar to air combustion [4]. Some part of the flue gas produced is recycled from downstream of the boiler before or after the condenser depending on wet or dry recycle requirement. The water vapour and other impurities produced in the combustion process is removed by dehydration and low temperature purification processes. A complete dehydration of the flue gas is important since it reduces mass flow and prevents hydrate precipitation and corrosion during pipeline transportation of CO_2 [18]. After the flue gas cleaning process, CO_2 concentration increases to above 90% in the exhaust gas that is ready for CO_2 capturing and sequestration [19, 5].

The flue gas consists of highly concentrated CO_2 stream and water vapour but also includes small amount of other gasses such as NO_x, CO, SO_x etc. depending on the fuel. OF technology enables capturing almost all CO_2 in the exhaust gas and the negligible amount of nitrogen in the oxidant reduces the formation of NO_x and amount of flue gas volume. Thus, much smaller flue gas cleaning equipment such as deNO_x and deSO_x are needed in OF combustion which reduces the capital and operating cost. The OF combustion operation is also flexible and able to operate in dual-firing capability which provides the possibility to switch to air-firing mode in the necessary circumstances [4, 19]. The main drawback of the OF combustion technology is the requirement for almost pure oxygen. The separation process in air separation unit to obtain high purity oxygen is energy demanding and thus expensive. One of the available large scale technologies to obtain a large quantity of high purity oxygen is cryogenic distillation. Furthermore, novel technologies such as membranes and chemical looping cycles are being studied and reviewed in several publications [20-22].

2.2. Oxy-fuel combustion versus air combustion

The replacement of air with the mixture of nearly pure O_2 and CO_2 rich recycled flue gas, causes several changes which are directly related to the combustion chemistry including ignition behaviour, flame characteristics and temperatures, heat flow, temperature profiles, pollutant formation and particle burnout. [4]. The differences in combustion characteristics between conventional air and OF combustion are mainly due to the distinction between thermo-physical properties of N_2 in air and CO_2/H_2O in OF combustion. The thermo-physical properties of these gases at 1123 °C are given in Table 1 [23, 24].

Table 1. Thermo-physical properties of gases at 1123 °C and atmospheric pressure.

Physical Property	**H_2O**	**O_2**	**N_2**	**CO_2**
Density (ρ) [kg/m^3]	0.157	0.278	0.244	0.383
Thermal conductivity (k) [W/m K]	0.136	0.087	0.082	0.097
Specific heat capacity (Cp) [kJ/kmol K]	45.67	36.08	34.18	57.83
Specific heat capacity (Cp) [kJ/kg K]	2.53	1.00	1.22	1.31
Mass diffusivity of O_2 in X (D) [m^2/s]	-	-	1.7×10^{-4}	1.3×10^{-4}

The absence of N_2 significantly increases the partial pressures of CO_2 and H_2O in the gas mixture which leads to enhanced radiative heat transfer due to a rise in gas emissivity [25]. It has been reported that, the changing of combustion environment from O_2/N_2 to O_2/CO_2 results in considerably lower temperature at the flame zone as well as a drop of the gas temperatures. This change also delays the ignition in the fuel particles. These are caused by the higher specific heat capacity of CO_2 and H_2O and also due to the lower diffusivity of O_2 in CO_2 compared to N_2 [26]. The knowledge about the effect of elevated CO_2 concentration on the ignition of the solid fuel particles and temperature profile of the furnace are important in order to understand how to switch existing burners from air to OF combustion conditions. Many studies have been performed for evaluating the influence of CO_2-rich environment. Among all these studies, Lie et al. reported a significant decrease in gas temperature and an longer coal ignition delay in O_2/CO_2 coal combustion due to the higher specific heat of CO_2 compared with that of N_2 [27]. Molina and Shaddix studied single particle experiments also on an ignition delay and it was reported that the ignition time got longer and combustion temperature reduced at the presence of CO_2 and lower O_2 concentration [28]. Additionally, tests with the application of switching the gas atmosphere from N_2 to CO_2 at constant molar fractions (21%O_2-79%N_2/CO_2) showed that the gas switching lowers the flame temperature and makes difficult stabilizing of the flame temperature in OF condition due to the differences in the thermo-physical properties of CO_2 and N_2 [29-31].

2.3. Oxy-fuel combustion characteristics

Combustion of the solid fuels such as coal, OS and biomass is a complex physical and chemical process. In order to understand how combustion characteristic of a solid fuel changes in OF combustion compared to conventional air combustion, behaviour of the fuel particles should be evaluated properly during the combustion process.

The combustible volatile matters and light hydrocarbon such as CH_4 and CO are released during devolatilisation and react with the oxidizer in the hot gas and burnt in the gas-phase. It is expected that the combustion of volatiles is affected by exchanging N_2 with CO_2 under OF combustion [32]. The diffusivity depends strongly on the temperature. The enhanced heat capacity of CO_2 leads to a drop in flame temperature for similar O_2 concentration of OF and air combustion. Accordingly, this reduction in the flame temperature reduces the burning rate. Thus, the consumption rate of volatile matters during OF combustion is slower than air combustion due to the lower diffusivity of small hydrocarbons in CO_2 compared to N_2. This situation could be improved in retrofit respects by having higher O_2 partial pressure and longer residence times owing to the lower gas volumetric flows during OF combustion [5, 29, 28]. During char combustion, the burning and heat generation rates in OF combustion reduces with the effect of exchanging N_2 for CO_2 because of the lower diffusivity of O_2 in CO_2 compared to N_2 [33]. In general, O_2 mole fraction of 0,3–0,35 yields similar temperature and burnout data for OF combustion compared to air combustion. Wang et al. indicated a remarkable increase in char burnout rate of pulverized coal by enhancing the O_2 concentration from 21% to 29% in OF combustion [34]. Therefore, the enhanced O_2 concentration in the oxidant for OF combustion compensates for the larger specific heat of CO_2 compared to N_2 and comparable burnout times are achievable in this way. Moreover, CO_2 and H_2O contribute to the burnout of char particles via gasification reactions together with the water gas shift reaction.

$$C + CO_2 \leftrightarrow 2CO \qquad (1)$$

$$C + H_2O \leftrightarrow CO + H_2 \qquad (2)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (3)$$

Recent studies of coal devolatilisation by Kumar et al. revealed that volatile yield in OF combustion was greater than in air due to the char gasification. The elevated CO_2 concentration surrounding the burning char particles led to the gasification reactions and thus reported as a contribution to the char mass loss [35].

2.4. Emissions during oxy-fuel combustion

Knowing the behaviour of the other non-CO_2 components such as SO_x, NO_x and trace elements during OF combustion is important since these components have an impact on the design of the power plant processes including flue gas cleaning equipment, construction and operation in various aspects.

High partial pressure of CO_2 and high temperature of combustion environment cause an increase in the CO emissions at the flame zone because of the thermal dissociation of CO_2 or the gasification reactions. The comparison of the CO emissions in OF and air combustion is important due to the severe toxicity of CO. Wang et al. conducted experiments with comparable flame temperature and reported no considerable difference in the CO concentrations both in the latter section of the flame zone and in the exhaust gas for OF and air combustion [34]. In addition, Woycenko et al. proposed a remarkable increase in CO levels within the flame zone but no significant CO emission was reported before the furnace exit due to the completion of CO combustion [36].

The reduction in NO_x formation was an important driver for research into OF combustion as there is higher formation of thermal NO_x in air combustion when more nitrogen is present in the combustion atmosphere [37]. However, results from the pilot-scale experiments showed an increase in concentration (ppm) of NO_x in the flue gas compared to the air-firing NO_x concentrations due to the recycling of NO_x in the flue gas back to the combustion chamber and a reduction in the total gas flow [38]. As a conclusion, the mass of NO_x released per energy generated is significantly less for OF combustion conditions with approximately one third of the total NO_x produced by air combustion [19].

In the case of SO_2 emissions, SO_2 in the flue gas of the pilot-scale experiments was found to be directly proportional to the fuel sulphur content in both OF and air combustion. However it was three times greater in OF combustion compared to air combustion in ppm level. The total mass (mg/MJ) of sulphur emitted during OF combustion was two-thirds of the total sulphur in the flue gas of air combustion and a very small additional decrease in mass of sulphur was observed when the recycle of flue gas through the furnace was increased [38]. Croiset and Thambimuthu indicated that the conversion of coal sulphur to SO_2 decreased from 91% for air combustion to 64% during OF combustion because of the sulphur retention by ash or deposits in the furnace [37]. Another research showed that the SO_2 concentration in OF combustion was found higher than air combustion due to the flue gas recirculation. Therefore, desulphurization unit for the RFG considered as a necessity in order to avoid corrosion of the furnace and the transportation system of CO_2 because of elevated SO_2 concentration levels in the flue gas [5].

In another research which was conducted by Zheng and Furimsky in order to assess the trace element emissions of coal combustion in O_2/CO_2 atmosphere, it was concluded that the combustion medium had little effect on the amount and type of the Hg, Cd, As and Se containing emissions in the vapour phase [39].

2.5. Combustion of blended fuels

Concerns regarding the global environmental impacts of fossil fuels used for power generation have promoted the development of more sustainable approaches. Increment in the fraction of renewable energy in the national energy supply is a remarkable solution to mitigate the adverse effects of power generation from fossil fuels. Co-combustion of biomass with fossil fuels such as coal and OS raises the share of renewable energy and co-combustion of waste contributes to minimize the hazardous effects of waste. The idea behind co-combustion is to burn different types of materials such as low and high grade fossil fuels, biofuels and waste in power plants at the same time. Biomass is the most common renewable and sustainable source of energy used in the co-combustion processes. Biomass can be defined as the carbonaceous organic material including the residues of agriculture and forestry, animal wastes and wastes from food processing operations. Biomass is considered as a form of stored solar energy and thus regarded as a clean and important energy source due to being completely CO_2 neutral, available abundantly, renewable and cost-effective solution to raise the share of renewable energy within a short term [40-44].

In the literature, there are numerous of studies on co-combustion of coal with wide diversity of biomass fuels. Alverez et al. carried out an experimental and numerical study concerning the co-firing of biomass with coal in an entrained flow reactor under different OF conditions and air condition. They reported that co-firing CO_2-neutral biomass with coals under OF conditions produced a below-zero CO_2 emission if the released CO_2 was captured and sequestered [45]. Varol et al. investigated co-combustion characteristics of various biomass fuels such as wood chips (WC), olive cake and hazelnut shell and different Turkish lignites by TGA between 25-1100°C with a heating rate of 20°C/min. They observed that ignition temperature decreased with a rise in the sample's volatile matter content [46]. Moon et al. studied the co-combustion of different ranks of coal and wood pellet (WP) using TG-DSC and it was concluded that blending WP with low-rank coal enhances the combustion efficiency by lowering ignition temperature with interaction effect and 10% biomass ratio was reported to have the remarkable impact [47].

There is also limited number of study available about the co-combustion of OS with different fuels including especially different types of biomass and SC. Kask et al. studied the co-combustion of OS and biomass in an environmental point of view in a pulverized-fired boiler operated at 30 MW capacity. The results indicated that the emissions of CO and total suspended particles diminished as the biomass ratio was raised in the blend. There were not any negative effects observed on the combustion process and boiler operation during the experiments [48]. Alar et al. tested co-combustion behaviour of OS and biomass in the full-scale CFB boiler. It was concluded that co-combustion of OS and biomass mixture lessened the CO_2 emission by 14.6% and ash formation by 16% when compared with conventional OS CFB combustion. Özgür et.al investigated the effect of co-combustion of biomass with OS using TGA and differential scanning method. It was concluded that biomass blended with OS in the ratio of 10% and 20% by weight was a good option for co-firing owing to the formation of a sufficient amount of volatile matter to maintain stability in ignition and combustion [49]. The research performed by Kuusik et al. to explore the optimum solution for treating and utilizing SC effectively and in an environmentally friendly manner showed that atmospheric CFB combustion technology with capturing the potential heat value of semi-coke is recommended as a feasible and an optimum technology [50]. Yang et al. investigated the co-combustion behaviors of Fushun low calorific OS and its SC using TGA method. The results showed that the increase on the OS mass fraction and oxygen concentration resulted in the improvements on combustion characteristics of the samples [51]. Qing et al. studied the kinetics and thermal characteristics of SC, sawdust and co-combustion of their blends at various mass ratios using a non-isothermal TGA. The study showed that the combustion performance of samples improved significantly with increasing sawdust proportion in the mixture [52]. Wang et al investigated the combustion of SC with rice straw using a TGA with heating rates of 10, 20, 50, 80 °C/min. from 40 to 900 °C. They observed the improvement in combustion owing to a decrease in ignition temperature and reported a more stable and reactive combustion process [53]. Furthermore, the combustion of SC with corn stalk was studied by Liu et al., using a TGA and several observed interactions found showing the increased reactivity during co-combustion [54].

2.6. Modeling of oxy-fuel combustion

Aspen Plus simulation software is one of the comprehensive tools to model combustion and the gasification characteristics of not only conventional fuels such as coal and biomass but also non-conventional fuels like OS. Aspen Plus is also used to predict the emissions of gaseous components for the modelled combustion and the gasification processes. The process simulation is created by specifying configurations of unit operations and the flow of material, heat and work streams.

There are several modeling studies mainly focusing on the conversion processes of solid fuels such as drying, pyrolysis and char combustion. Xiong et al. simulated and analysed OF combustion in pulverized-coal-fired power plant using Aspen Plus software in order to study the operation characteristics of the OF combustion process. The simulation results indicated that Aspen Plus was a proper tool to analyse the OF combustion system. Furthermore, many parameters and different cases were also investigated and the results showed that recycle ratio range proposed for cold recycle cases was higher than that of recommended for the hot recycle case. It was reported that the CO_2 concentrations in the flue gas range from 84 to 92 mol % for cold recycle cases and from 57 to 58 mol % for hot recycle cases because of the high H_2O content, respectively. In addition, OF cases had higher SO_x fractions but a similar unit of the SO_x production rate and much lower NO_x fractions in the flue gas as compared to air combustion [55].

Pei et al. built up a process simulation of OF combustion for a pulverized coal-fired power plant using Aspen Plus software to identify the differences between air and OF combustion processes and also to examine the influences of temperature, excess oxygen ratio and molar fraction of O_2/CO_2 on the proportions of different components in flue gas by sensitivity analysis. It was proposed with the process simulation results that replacing atmospheric air by 21%O_2/CO_2 mixture resulted in a decrease in the flame temperature. Furthermore, the equilibrium amount of NO_x declined obviously but the SO_x remained at the same level. The mass fraction of CO_2 in the flue gas was found to increase from 21.3% to 81.5%. The amount of NO_x was affected sensitively by the change of temperature and the excess oxygen ratio. The flame temperature and NO_x emission enhanced rapidly with the increasing of O_2 concentration. When the molar fraction of O_2 increased to 30%, the flame temperature settles at a similar value in the air atmosphere [56]. A process simulation model was proposed by Dong et al. to predict the combustion of coal in a CFB boiler with Aspen Plus. The effects of coal feed flow rate, the temperature of preheated air and air flow rate on the exhaust gas temperature were analysed. They reported similar exhaust gas temperature and boiler efficiency with the previous data from literature [57].

OS combustion processes and its thermal processing were simulated with Aspen Plus in very few studies so far as it is challenging to define the OS in Aspen Plus due to its complicated chemistry. Therefore, OS must be defined as a non-conventional fuel under mixed sub-streams including liquid, gas and solid components. Sherritt et al. simulated a steady-state process model for retorting of the Green River OS using Aspen Plus. Aspen Plus was declared as a beneficial process simulator for the development of an OS conversion process and created operations were found adequate for steady-state models [58, 59]. Furthermore, Yörük et al. simulated the OS combustion processes of EOS with the recently released FB reactor of Aspen Plus and also with the equilibrium based model. First model determined the required elutriated mass flows in CFB processes and it was reported that the CFBC simulation predicts the solids density of the bottom bed and splash zone. However, it does not allow the reasonable prediction of the solids concentration in the transport zone owing to the single entrainment correlation which can be a limitation of the current Aspen FB modeling block [60]. Second model predicts the flue gas composition of OS combustion in OF cases with wet and dry FGR [61]. The applied modeling approach demonstrated that it is possible to achieve similar temperatures in the simulated cases and above 840°C, NO_x and SO_x emissions are in an increasing trend.

2.7. Aim and scope

There is valuable information in the literature related to the differences between air and OF combustion processes and co-combustion of conventional fuels like coal and biomass. Based on the discussed literature data it can be understood that the use of multi fuel concept to generate heat and electric power strongly influences the combustion process, due to the different elemental and mineral composition of blended fuels. The overall capacity, efficiency of the boiler and the flue gas emissions are strongly dependent on the fuel mix. Consequently, it is a major challenge to be able to control all these aspects below their given limits or in required levels for all different fuel combinations in the mixtures. Furthermore, the concept of OF combustion technology brings additional research questions and increases the importance of the studies with unconventional fuels like OS with high mineral carbonate (i.e. CO_2) content. However, there are very limited studies related to OS and similar type of fuels. Among the latest publications concerning OS and, particularly EOS, valuable insights for the realization of OF combustion of EOS can be found from both experiment and modeling studies which show that the application of OF combustion to EOS and similar type of carbonate rich fuels can be done without having any fundamental difficulties. However, the combustion mechanism and characteristics of the co-combustion of EOS with biomass and SC can be strongly different from the solely EOS case. Thus, there is a necessity to carry out a fundamental research on co-combustion characteristics of EOS with biomass and SC in OF conditions to better understand the interactions between these different fuels. The boiler temperature regimes which have to match with the thermal design of air combustion and flue gas compositions depending on the different blend ratios provide also important knowledge to support the designers and operators when they evaluate the feasibility of different fuel blends in their installations.

In this point, the aim of the current master thesis is to obtain fundamental technical knowledge related to the above mentioned issues by investigating the co-combustion characteristics of EOS with biomass and SCE. The research in this thesis includes both experimental and process modelling work. Thermal behaviour of EOS and SCE, pine saw dust (PSD) and blended fuels was studied with the Setaram Setsys Evo 1750 thermoanalyzer and different co-firing cases were simulated using the ASPEN PLUS V8.6 (APV86) software tool to characterize the process specifics under air and OF combustion conditions.

The following topics were the main subjects studied and discussed in this work:

Experimental

- Comparison of thermal behaviour of EOS, SCE, PSD fuels and their selected blends under 21%O_2/Ar and 30%O_2/CO_2 atmospheres;
- Effect of biomass and SC on OS oxidation characteristics and kinetics;
- Effect of biomass and SC on the stages of EOS combustion including its mineral part.

Process Modeling

- Calculation of boiler temperatures for the simulation cases with the same thermal load by adjusting fuel input;
- Estimation of the composition of flue gas by calculating mass–energy balance and chemical equilibrium of the processes;
- Effect of different fuel ratios in the blends on the flue gas composition;
- Effect of boiler (combustion) temperature on the flue gas composition.

3. EXPERIMENTAL AND MODELING

3.1. Materials and methods

Fuel Samples

Three different types of solid fuels including EOS, one type of biomass, namely pine sawdust (PSD), and semi-coke of Estonian oil shale (SCE) were selected for thermal analysis (TA) experiments. The OS sample used in the experiments was obtained from Estonian Energy Company (from the Enefit 140 process). The pine sawdust samples were obtained from a local manufacturer using pine tree growing naturally in Estonia.

Preparation and Characterization of Samples

PSD was ordered in fine fraction from a local supplier using sawmill, yet EOS and SCE samples were crushed with an alligator-type grinding machine. The mean sample was then taken from the crushed sample and ground in a big ball mill. Subsequently, EOS and SCE samples were dried at 105°C for 4 hours and ground also in a Retsch PM 100 grinding machine in a four-ball planetary mill (20 minutes at 350 rpm, revers 5 min) until all sample passed through a 200 µm sieve. PSD, as received, dried at 105°C for 4 hours and later sieved (through a 200 µm sieve) to obtain similar size fraction for the TG/DTG/DTA and kinetic tests.

The mixtures (EOS/SCE, EOS/PSD and EOS/SCE/PSD) were prepared in desired fraction and Retsch PM 100 grinding machine was used additionally to make the mixtures more homogeneous. SCE and PSD added to EOS in ratios of 20 and 40% in mass basis (80:20, 60:40) and a mixture of EOS/SCE/PSD was prepared in the ratio of 70:15:15.

The fuel characteristics of the samples are listed in *Table 2*. It can be seen from the table that the higher heating values (HHV) of fuel samples are different from each other. PSD has the highest HHV due to the higher organic (volatile) content of PSD compared to EOS and SCE. In addition, PSD contains more carbon that is almost 1.5 times higher than EOS and hydrogen content which is two times higher as compared to EOS. SCE has the lowest HHV, carbon and hydrogen content among the samples. EOS and SCE samples have higher content of carbonates and mineral matters thus, the mineral CO_2 content of EOS and SCE are 18.55 and 24.70%, respectively.

Table 2: Characterization of fuel samples.

	EOS	SCE	PSD
HHV (as received), MJ/kg	10.3	1.96	19.43
	Content, % mass		
Moisture (as received)	11.00	0.10	2.50
N^d	0.05	0.04	0.18
C^d	30.20	11.65	48.92
H^d	3.30	0.229	6.12
S^d	1.50	2.153	0.005
TC	32.03	12.18	-
TIC	5.06	6.75	-
TOC	26.97	5.43	-
CO_2^M from TIC	18.55	24.70	-

^{d} Per dry sample, ^{M} mineral CO_2,

Experimental methods

TA experiments were conducted with Setaram Setsys Evo 1750 thermoanalyzer to investigate the oxidation and decomposition characteristics of EOS, SCE, PSD and their blends in different atmospheres. During the experiments, standard 100 μL Pt crucibles were used and 20±0.5 mg of the sample was weighted. The non-isothermal tests were performed at 10 K/min heating rate up to 1000 ºC and total gas flow rate was set to 30 ml/min. The specific gas atmospheres for air and OF conditions were created by mixing two gas streams at the desired fractions and 21%O_2/Ar and 30%O_2/CO_2 mixture of stream were used during the experiments for the modeling of air combustion and OF combustion, respectively.

AKTS Advanced Thermokinetics software was used to calculate the kinetic parameters for the oxidation stages of EOS, EOS/SCE and EOS/PSD blends in the ratio of 80:20 by wt.% in 21%O_2/Ar. A model-free approach based on differential iso-conversional methods was applied to calculate the conversion-dependent activation energies. For detailed information on kinetics calculations see references [62, 63].

3.2. Modeling approaches and descriptions

Different cases of EOS co-combustion with different biofuels and SCE were simulated using the ASPEN PLUS V8.6 (APV86) software tool for modeling air and OF combustion conditions. As a main modeling strategy, OF combustion cases were simulated with dry and wet FGR strategies by controlling the O_2 percentage in flue gas based on maintaining similar temperatures for gas-solid mixture at the outlet of combustion reactor, similar to the temperature at air combustion. The main target was to evaluate the effects of blending EOS with other fuels regarding the operation conditions of air and OF combustion and calculate the specific boiler temperatures *with the same thermal input*. Later, the estimation of the composition of flue gas by calculating mass–energy balance and chemical equilibrium of the processes was also made *with same fuel flow rate* for different blending ratios. For this purpose, simulations were built up for wide range of mixing ratios for investigating the effects of biomass and SC on the specific gaseous emissions such as SO_x, NO_x as well as CO_2 and the ash formation. Finally, the temperature effect on gas emissions (CO, SO_2, NO, NO_2 and CO_2) in air and OF atmosphere was investigated by sensitivity analysis. The simulated processes are at steady state and isothermal conditions. The simulations have been built up based on the material balance, energy balance and chemical equilibrium relations. *Table 3*, shows the compositions of EOS and SCE while *Table 4*, lists the compositions of WP, WC and PSD considered in the simulations. EOS and SCE fuels were defined as a mixture of organic matter, the most important minerals and moisture (as free water) under different sub-streams. The selected minerals such as $CaCO_3$, $MgCO_3$, SiO_2 and FeS_2 were defined at the specific proportions for EOS and SCE. The defined EOS contains 27% organics, 62% mineral part and 11% moisture. The SCE has the lowest HHV and it contains the least organics and highest mineral part in the fuels used in the simulations.

Table 3: Compositions of EOS and SCE.

	EOS	**SCE**
Organic (%)	27	4.2
C	77.45	11.65
H	9.7	0.23
N	0.33	0.04
S	1.76	2.15
O	10.01	85.93
Cl	0.75	-
Mineral (%)	62	95.8
$CaCO_3$	57.9	55
$MgCO_3$	7.1	5
SiO_2	30.2	40
FeS_2	4.8	-
Moisture (%)	11	0.1
HHV (MJ/kg)	10	1.96

The ash content of biomass fuels (WP, WC and PSD) was considered as completely solid ash from Aspen database instead of including individual minerals. The data for WP and WC was taken from BIODAT database [64]. WP contains the highest organic matters and the lowest ash content compared to other fuels. The defined PSD has the highest HHV and WC has the lowest HHV. WC contains 43.5% moisture that is the highest water content compared to other fuels used in the simulations.

Table 4: Compositions of WC, WP and PSD.

	WC	**WP**	**PSD**
Organic (%)	55	94.66	87.5
C	50.29	50.8	48.92
H	6.7	7.51	6.12
N	0.1	0.03	0.18
S	0.01	-	0.005
O	42.9	41.67	44.78
Cl	-	-	-
Moisture (%)	43.5	4.9	2.5
HHV (MJ/kg)	9.6	18.07	19.43

Air combustion was simulated with 20% excess air and OF combustion was simulated with an 3% excess amount of O_2 in the flue gas. *Figure 5* presents the process flow diagram of OF combustion for simulation model. The combustion modeling consists of organic part decomposition for all fuels which was simulated with RYield reactor. In this reactor, organic matter of the fuel was converted into its constituting components including carbon, hydrogen, oxygen, sulfur, nitrogen and chlorine by specifying the yield distribution based on the ultimate analysis of the fuel. Later, RGibbs reactor was used for the equilibrium based calculations. The total Gibbs free energy of the system can be shortly defined as follows [65]:

$$G^t = \sum_{i=1}^{N} n_i \, \mu_i \tag{4}$$

Where G^t is the total Gibbs free energy, n_i the number of moles of species i, and μ_i the chemical potential of species i.

Several compounds were particularly considered during combustion simulations based on the fuel characteristics of EOS, SCE, WC, WP and PSD. The defined components as gas or solid products in the Gibbs reactor are given in *Table 5*.

Table 5: Gas and solid products defined in the Gibbs reactor.

Gases	**Solids**
CO_2, CH_4, CO, H_2S, SO_3, SO_2, NO_2, NO, N_2, O_2, HCl, H_2, H_2O, S, Cl_2	C, $CaCO_3$, $MgCO_3$, SiO_2, FeS_2, CaO, MgO, $MgSO_4$, $CaSO_4$, $FeSO_4$, Fe_2O_3

Solid ash formed with the reactions in the RGibbs reactor is separated from the flue gas by the splitter (cyclone). The specified fraction of the flue gas is recycled back into the furnace during the OF combustion cases. Both dry and wet FGR cases (*Fig. 5*) are considered with the constant temperature (250°C).

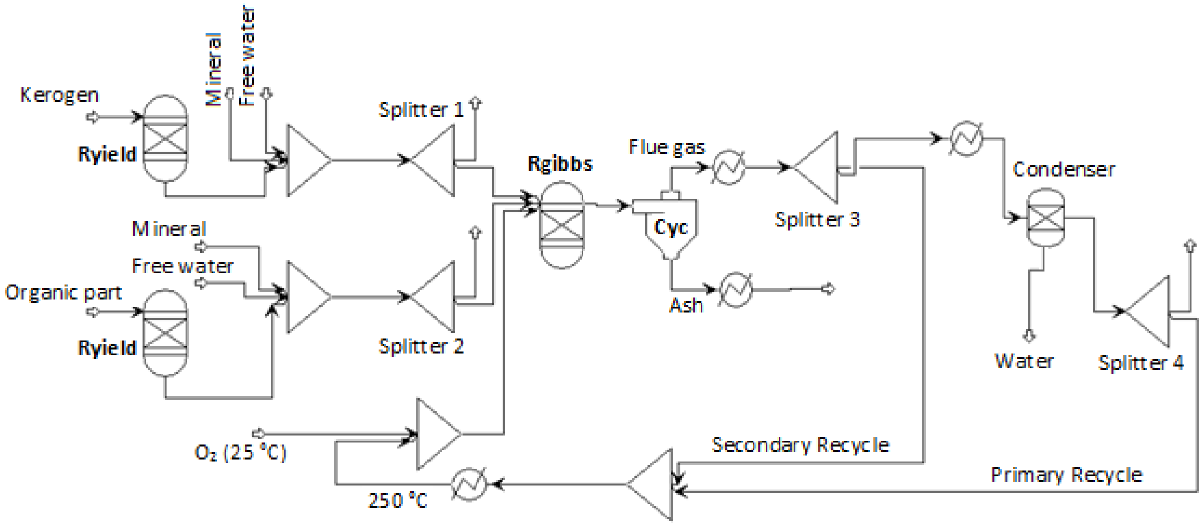

Figure 5: Process flow diagram of OF combustion for simulation model.

4. RESULTS AND DISCUSSION

4.1. Thermal analysis and kinetics

TA of EOS, PSD, SCE and their blends have been presented using TG (mass change, %), DTG (mass change rate, % min $^{-1}$) and DTA (heat effect, μV) profiles under air (21%O_2/Ar) and OF (30%O_2/CO_2) atmospheres. The results of kinetic calculations of oxidation process for EOS, EOS/SCE and EOS/PSD are reported in 21%O_2/Ar and presented via conversion-dependent activation energy curves.

EOS, PSD, SCE samples and their blends in 21%O_2/Ar

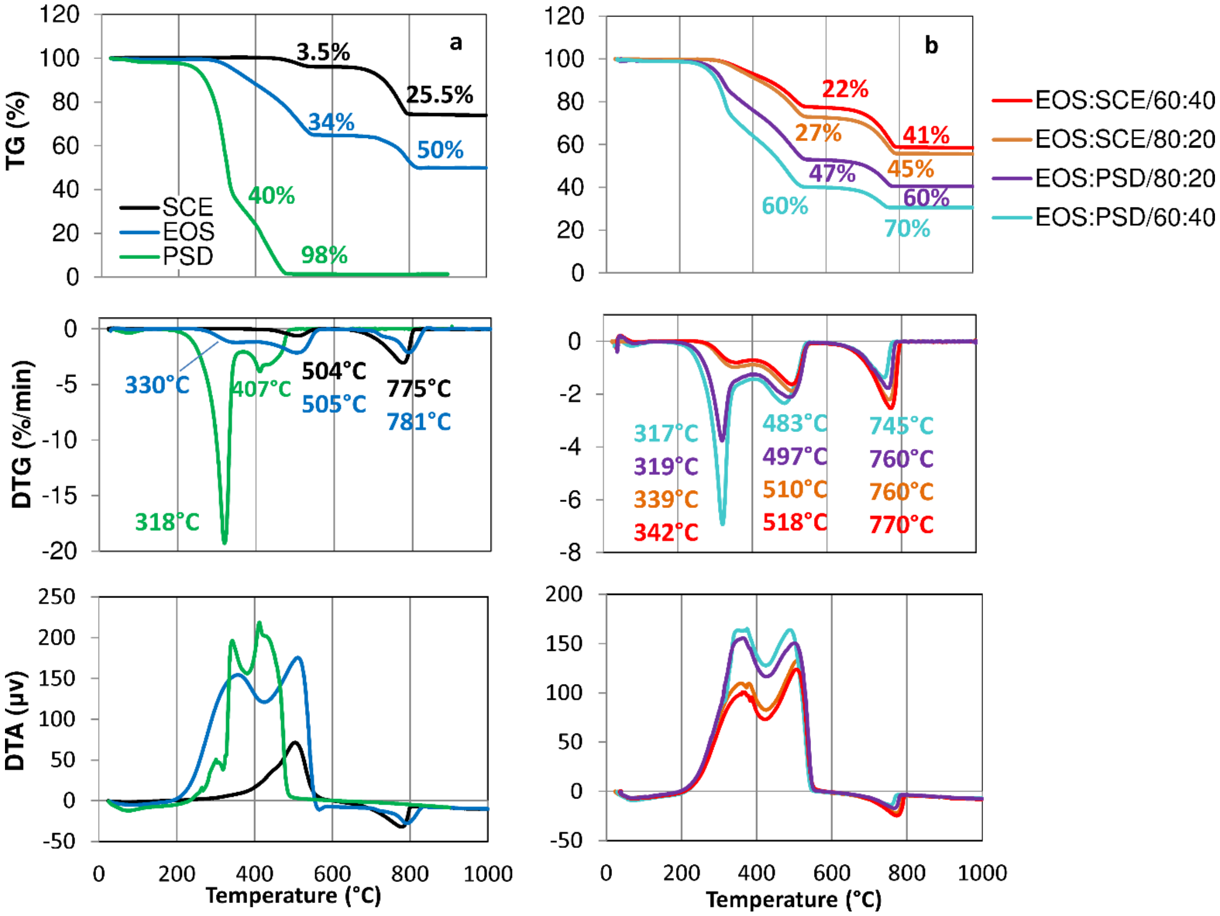

Figure 6: Comparison of the individual samples (a) and their blends (b) in 21%O_2/Ar based on TG, DTG and DTA.

Figure 6, shows the results of TA experiments for the EOS, PSD and SCE (Fig. 6a) as well as their prepared blends in defined ratio (80:20 and 60:40 % by weight) (Fig. 6b) in 21%O_2/Ar atmosphere. As can be seen from the *Figure 6a*, the first mass loss and the endothermic heat effect observed clearly for the PSD and also slightly for other samples as well between 0°C and 150°C is the moisture release. After the evaporation of moisture, EOS and PSD reach to the devolatilization stage, which is followed by volatile combustion and char oxidation processes. On the DTA curve of PSD and EOS samples, two distinctive and intense exotherms (corresponding to the oxidation of volatile components and char oxidation, respectively) can also be seen. The effect of retorting is clearly seen as there is no any visible devolatilization stage. Thus, SCE has only one peak on the DTA and DTG at 504°C which is also represented with small and single step on TG which is related to the char oxidation step between 450°C-540°C.

EOS and SCE sample has two distinctive mass loss steps (Fig. 6a) one in the low temperature zone between 270°C and 560°C and additional thermal decomposition at higher temperature zone between 650°C and 830°C. Endothermic effect can clearly be seen for the second mass loss step due to the endothermic decomposition of $MgCO_3$ and $CaCO_3$ in EOS and SCE indicating a wide endothermic effect The temperature obtained from DTG maximum and endotherm for the second step mass loss step of SCE (775°C) is slightly lower than EOS (781°C), which can related to the retorting process of SCE.

There is very sudden transition from devolatilization stage to char oxidation stage for PSD sample, and above 480°C there is no further visible exotherm or endotherm. Until char oxidation stage there is almost 58% mass loss related to the volatile content of the PSD and almost 98% of the total mass of PSD (38% - fixed carbon) has been lost during the oxidation stage in 21%O_2/Ar between 220-480°C. According to the oxidation stages shown in *Figure 6a*, almost 50% of total mass (35%+15%) has been lost during the combustion process of EOS in 21%O_2/Ar atmosphere. SCE consists of less organic matter and considerably high amount of mineral matters compared to other samples. Thus, the first mass drop shown in *Figure 6a* was 3.5% which was related to the oxidation of char and total mass loss with the decomposition of carbonates (660°C-800°C) reaches to 25.5% in 21%O_2/Ar atmosphere.

In the case of blended fuels (Fig. 6b), the co-firing of EOS with PSD influences the combustion process while lowering the ignition temperature and enhancing the combustion, due to high volatile and oxygen content of PSD which makes the ignition of the blended samples easier than the EOS alone. The DTA curves show that the heat effect during oxidation processes is enhanced as the mass ratio of PSD is increased, due to the higher energy intensity of the PSD sample on a mass basis.

There is a shift to lower temperatures on DTG maximums with higher ratios of PSD in the blends. Contrary, there are higher maximum reactivity temperatures and lower mass loss rates for EOS/SCE blends compared to EOS and EOS/PSD due to the low volatile content and high mineral matter in the blended fuels. As it can be seen from DTG curves, addition of PSD to EOS increases the rate of mass loss especially during the early stages of oxidation process due to the high volatile and oxygen content of the PSD which can be considered as positive interaction between these fuels. It can be seen that, as the PSD ratio in the blends is raised, total mass loss in both atmosphere is increased. Likewise, as the PSD ratio greater in the blend, the ash content of each blend reduced owing to the lower ash content of PSD sample. The residual mass is higher for the blends with SCE due to the high mineral content and low ash content in PSD.

There is no evidence for any significant synergetic effects between either PSD or SCE during the co-combustion with EOS as the mass loss behaviour of the blends reflects the behaviour of the individual materials, depending on the blending ratios. However, decomposition temperatures of $MgCO_3$ and $CaCO_3$ are shifted to lower temperatures especially for EOS/PSD due to the lower partial pressure of CO_2 in the atmosphere compared to the other blends and single EOS, SCE samples. The catalytic effect between alkalines in PSD ash and carbonates can also be another reason as biomass fuels are rich in alkaline metals (potassium, phosphorus, chlorine and sodium) which form complex eutectic salts that effectively lower the calcination point during the combustion [66].

EOS, PSD, SCE samples and their blends in $30\%O_2/CO_2$

Figure 7, shows the results of TA experiments for the EOS, PSD and SCE (Fig. 7a) as well as their prepared blends in defined ratio (80:20 and 60:40 % by weight) (Fig. 7b) in $30\%O_2/CO_2$ atmosphere.

The first weak mass loss step between (0-150°C) is the moisture release for all samples. The most important difference between $21\%O_2/Ar$ and $30\%O_2/CO_2$ atmospheres is the third mass loss step of EOS and SCE samples (their blends as well) which is related to the different behaviour of carbonates in the mineral part of these fuels under the CO_2-rich atmosphere. The decomposition of $MgCO_3$ and $CaCO_3$ is shifted a part and proceeds with maximum rate at 752°C and ≈902°C, respectively for both EOS and SCE (Fig 7a) due to high CO_2 partial pressure in $30\%O_2/ CO_2$.

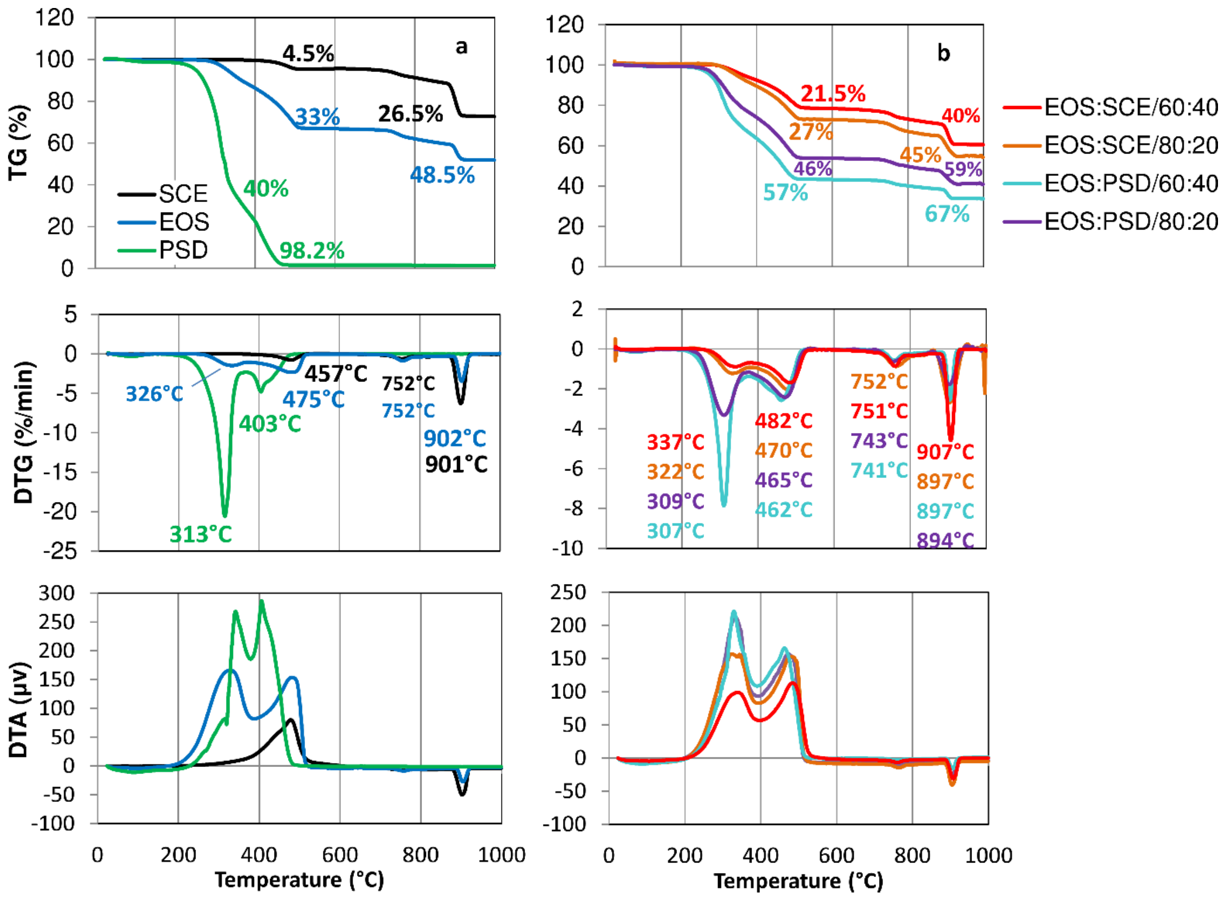

Figure 7: Comparison of the individual samples (a) and their blends (b) in 30%O_2/ CO_2 based on TG, DTG and DTA.

The mass loss steps of EOS shown in *Figure 7a* are originated from first the devolatilization and oxidation of the organic matter followed by the separated decomposition of the mineral part of the EOS sample. The total mass loss of EOS in these steps between 300°C and 920°C is 48.5% which is very close to the value at 21%O_2/Ar atmosphere. The total mass loss of PSD between 220°C and 470°C is 98,2%, that is also similar to the value at 21%O_2/Ar atmosphere. SCE has 26.5% total mass loss between 450°C and 920°C which is almost equal to the value under 21%O_2/Ar atmosphere. Total mass loss of blended samples with 20% wt. and 40% wt. SCE in *Figure 7b* was found as almost similar 41% and 40% in 21%O_2/Ar atmosphere, and they are 40% and 45% in 30%O_2/CO_2 atmosphere, respectively. For EOS/PSD blends in the ratio of 20% and 40% by wt. have 60% and 70% mass loss in 21%O_2/Ar atmosphere as well as 59% and 67% in 30%O_2/CO_2 atmosphere, respectively. Small differences in these values can be related to the non-homogenity of the sample.

Similar to the 21%O_2/Ar atmosphere, blends with SCE has also higher ash residue due to the high amount of minerals in SCE. In summary, the results of TA tests for all samples in

$30\%O_2/CO_2$ atmosphere are similar to the results at $21\%O_2/Ar$ atmosphere in terms of amounts of oxidizing matter. However, the peak temperatures obtained from the DTG maximums of the oxidation stages of all samples are shifted to lower temperatures compared to those in $21\%O_2/Ar$ atmosphere due to higher O_2 concentration in $30\%O_2/CO_2$ atmosphere.

EOS sample and EOS/SCE/PSD blend in $21\%O_2/Ar$ and $30\%O_2/CO_2$

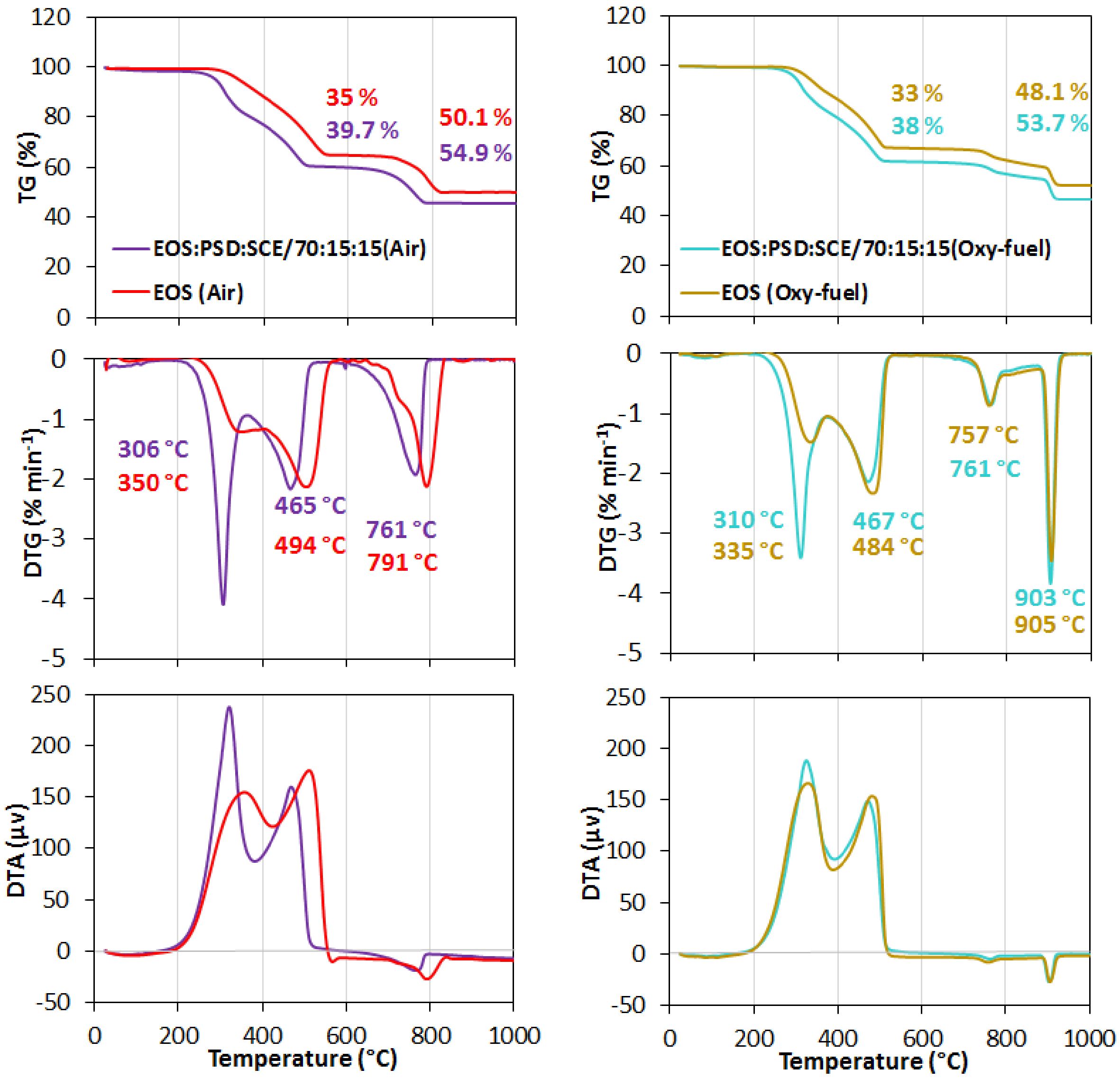

Figure 8: Comparison of the EOS and EOS/SCE/PSD samples in $21\%O_2/Ar$ (a) and $30\%O_2/CO_2$ (b) based on TG, DTG and DTA.

Figure 8, shows TG, DTA and DTG profiles for the blended fuel including three samples (EOS, SCE and PSD in the ratio of 70%, 15% and 15% by wt.). During oxidation and mineral decomposition processes of the blended samples, the total mass loss in $21\%O_2/Ar$ and $30\%O_2/CO_2$ atmospheres are 54.9% and 53.7%, respectively. In general, similar effects are existing also for this blended sample. As can be seen form *Figure 8*, the blended fuel including three samples showed almost similar characteristic temperatures to single EOS fuel sample in both organic and mineral parts, this similarity was more obvious especially in 30%O_2/CO_2 atmosphere. Furthermore, with the EOS:SCE:PSD there is less ash residue compared to the EOS.

Kinetic calculations

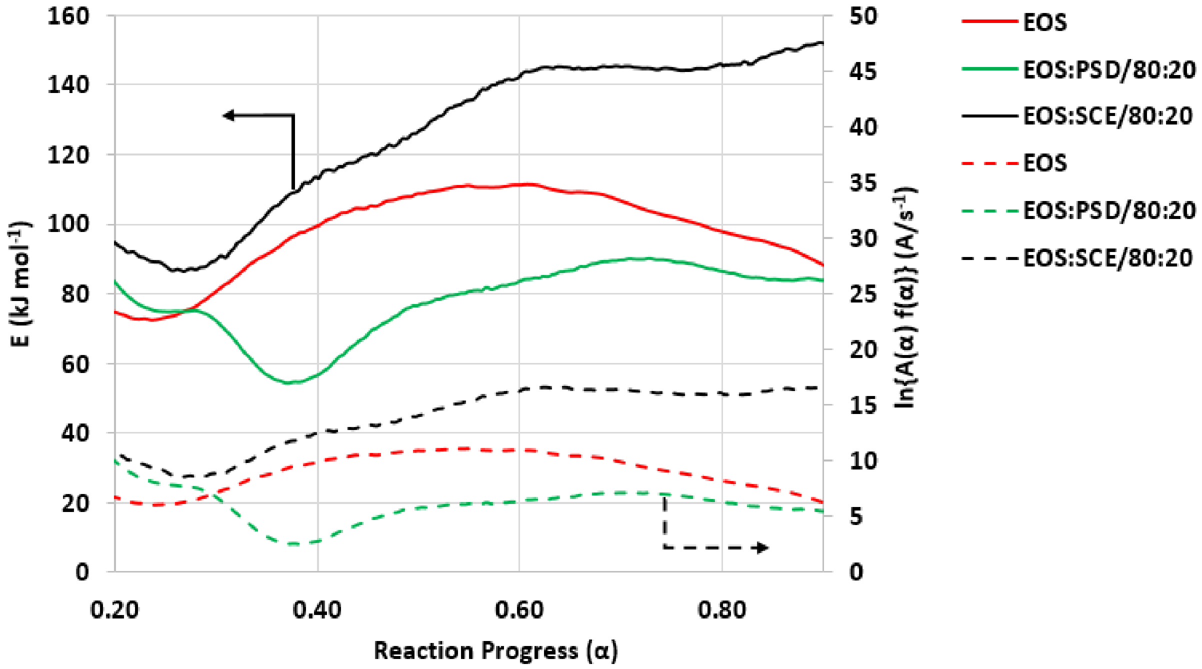

Figure 9: Conversion-dependent activation energy (E) and logarithm of pre-exponential factor (A) for EOS, EOS/SCE (80:20) and EOS/PSD (80:20) samples in 21%O_2/Ar atmosphere.

Considering the oxidation stage of overall process, *Figure 9* presents the conversion-dependent activation energy, E and logarithm of pre-exponential factor calculations for EOS, EOS/PSD (80:20) and EOS/SCE (80:20) blends in 21%O_2/Ar atmosphere.

As can be seen that apparent activation energy of EOS sample is in between 73-110 kJ/mol, for the reaction progress range, α= 0.2-0.9. Activation energy of EOS is at lower values about 75 kJ/mol (devolatilization stage) at the beginning of the oxidation stage. Subsequently, it is increasing gradually till its maximum value (110 kJ/mol) due to the char related reactions later activation energy diminishes to 90 kJ/mol. For the EOS/PSD (80:20), the calculated apparent activation energies are lower than the calculated values for EOS (between 54-90 kJ/mol). However, during the initial stage of the oxidation process there is slightly higher values (85-75 kJ/mol). Further there is sudden decrease (at α=0.35) on the results with the reaction progress later it is again increased at the final stage of oxidation process of EOS/PSD sample. Apparent activation energies for the EOS/SCE (80:20) sample have the highest values between 87 and 150 kJ/mol. At the first stage of oxidation process, similar to the other samples, there is a slight decrease on the activation energies. As the reaction progress increased activation energy values start to rise continuously till α=0.6. For the final stage (between α=0.6 and 0,8) activation energies remain constant and increase slightly at the very last stage. The trend in the change of the logarithm of pre-exponential factor for all samples is similar to the apparent activation energy curves with respect to reaction process.

4.2. Modeling results

Table 6, shows the selected simulation results for air and OF combustion of EOS and its blends with WC, WP, PSD, SCE. For all the simulated OF cases, it is possible to reach similar temperature levels as it is in air combustion case by increasing O_2 concentration to almost 30%O_2 levels. O_2 concentrations are slightly higher with the dry FGR method compared to wet and the EOS/SCE case has the highest O_2 concentration (31.6%) among other cases. The highest calculated boiler temperatures are 1734°C and 1722°C for EOS/WP and EOS/PSD cases, respectively and these temperatures are almost 200°C higher than the boiler temperature calculated for the single EOS case. The closest calculated temperatures to EOS case (1546°C) are in EOS/WC/SCE (1534°C) and EOS/WP/SCE (1658°C) cases showing that these fuel blends can be a good alternative to single EOS combustion providing similar boiler temperatures. Besides, flue gas flow rate values are also quite similar in these two cases compared to the EOS case, showing that temperatures both in the boiler and convective pass can be stabilized and maintained in similar temperatures regimes. Although EOS/WC/SCE case has the lowest FGR ratio 59% for dry and 61% for wet cases, there is similar amount of flue gas flow rate due to the high moisture content in WC fuel. The high moisture content of biomass reduces the boiler temperature and makes it more difficult to sustain the similar temperature level with the optimum FGR ratio which is generally considered as almost 65% in terms of flame stability and released heat of energy in convective pass of CFB boilers. The conditions in EOS/PSD and EOS/WP have the lowest moisture content in the flue gas composition which also leads to the highest obtained temperatures and FGR ratios compared to other simulated cases. In the case of using high moisture content biomass fuels, O_2 concentration can be increased and excess O_2 can be fixed as maximum 5% in order to increase the FGR ratio to the critical points. This can also increase the furnace temperature, reaction rate, and decrease the ignition delay, improves fuel drying and solves the problem of unstable flame.

There is a notably higher ash flow rate in OF combustion cases especially for the cases with blended with SCE. Dry and wet FGR have no particular effect on the ash flow rate and composition. EOS/WC in OF case (49.3 kg/s) has the closest ash flow value to EOS air-firing case (48 kg/s). WP and PSD have a major effect on the ash flow rates by reducing almost 30% in both air and OF cases. The high level of $CaCO_3$ decomposition in the air combustion cases keeps the ash flow rate in low values, yet there is an opposite effect for the OF cases as most of the $CaCO_3$ stays undecomposed at 810°C due to the higher partial pressure of CO_2. Therefore, optimum blending with biomass can compensate the increased ash flow rate which can also give flexibility to changes that might occur in the heat and mass balance of the system during the system transition from air to OF combustion.

As it can be seen from the EOS/WP/SCE and EOS/WC/SCE cases that ash flow rates can also be kept even lower and similar to air EOS case depending on the biomass types and ratio of the utilized SCE as well. Although the low heating value and high carbonate content of SCE brings along endothermic decomposition of carbonates affecting negatively the heat balance and ash flow rates, firing of EOS with specifically selected blend ratios for biomass and SCE under OF conditions can give an effective solution for the parameters related to the heat and mass balance, reduction of CO_2 emissions and also for the utilization of the heating value of SC.

Table 7, shows some of the physical properties of the flue gas mixtures including the heat capacities, flow rates as well as densities of flue gases and physical properties of oxidants for EOS and its different blends in air and OF cases. As seen in the table, densities of flue gas in OF conditions are higher than air for all cases. Similarly, heat capacities of both flue gases and oxidants are always greater in OF conditions. Depending on the unit of heat capacities (whether mass or mol basis) there is slight difference between the dry and FGR cases.

Table 6: Selected simulation results for air and OF combustion of EOS and its blends with WC, WP, PSD, SCE.

	Air EOS	**OF EOS**		**Air EOS/WC**	**OF EOS/WC**		**Air EOS/WP**	**OF EOS/WP**		**Air EOS/PSD**	**OF EOS/PSD**	
Blend ratio	**-**	**-**	**-**	80/20	80/20	80/20	80/20	80/20	80/20	80/20	80/20	80/20
Thermal load of fuel input, MW	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
Fuel flow rate, kg/s	100	100	100	100.8	100.8	100.8	86.1	86.1	86.1	84.1	84.1	84.1
FGR option	-	Dry	Wet	-	Dry	Wet	-	Dry	Wet	-	Dry	Wet
Temperature, °C	1546	1546	1546	1598	1598	1598	1734	1734	1734	1722	1722	1722
FGR ratio, %	-	62.6	64.4	-	60.5	62.4	-	63.1	64.5	-	63.0	64.4
O_2 concentration, % Vol	21%/N_2	30.6	29.0	21%/N_2	29.8	28.2	21%/N_2	29.7	28.4	21%/N_2	29.7	28.5
Flue gas flow rate, kmol/s	14.9	10.2	10.8	15.7	11.2	11.8	15.2	10.9	11.4	14.02	9.96	10.40
Flue gas composition at 810 °C, % Vol												
CO_2	14.4	77.9	63.7	13.9	75.4	60.3	14.2	78.5	64.9	14.6	78.9	65.8
H_2O	12.7	18.5	32.7	15.2	21.2	36.3	12.8	18.0	31.6	15.5	17.6	30.7
NO_2 (ppmv)	27.9	1.5	1.3	28.2	1.3	1.24	29.7	1.29	1.17	29.4	1.52	1.39
SO_2 (ppmv)	0.12	0.18	0.15	0.11	0.18	0.14	0.11	0.18	0.15	0.11	0.18	0.15
CO (ppmv)	0.07	0.35	0.29	0.07	0.35	0.28	0.07	0.36	0.29	0.07	0.36	0.30
Ash flow rate, kg/s	48.0	60.8	60.8	39.0	49.3	49.3	33.1	41.9	41.9	34.0	42.6	42.6
Ash composition, % mass												
$CaCO_3$	0	47.6	47.6	0	47.4	47.4	0	47.6	47.6	0	45.8	45.8
CaO	33.8	0	0	33.5	0	0	33.7	0	0	32.1	0	0
$CaSO_4$	18.2	14.4	14.4	18.1	14.3	14.3	18.2	14.4	14.4	17.3	13.8	13.8
Fe_2O_3	4.1	3.2	3.2	4.1	3.2	3.2	4.1	3.2	3.2	3.9	3.1	3.1
Wood ash	-	-	-	0.77	0.61	0.61	0.22	0.18	0.18	4,9	3.9	3.9
Recycled flue gas composition, % Vol												
CO_2	-	95.6	72.4	-	95.8	70.1	-	95.8	73.8	-	95.8	74.5
H_2O	-	0	23.6	-	0	25.9	-	0	22.3	-	0	21.6
Other	-	4.4	4	-	4.2	4	-	4.2	3.9	-	4.2	3.9

Table 6 (continued)

	Air	OF		Air	OF		Air	OF	
	EOS/SCE	EOS/SCE		EOS/WP/SCE	EOS/WP/SCE		EOS/WC/SCE	EOS/WC/SCE	
Blend ratio	80/20	80/20	80/20	70/15/15	70/15/15	70/15/15	70/15/15	70/15/15	70/15/15
Thermal load of fuel input, MW	1000	1000	1000	1000	1000	1000	1000	1000	1000
Fuel flow rate, kg/s	119.1	119.1	119.1	99.95	99.95	99.95	114.5	114.5	114.5
FGR option	-	Dry	Wet	-	Dry	Wet	-	Dry	Wet
Temperature, °C	1461	1461	1461	1658	1658	1658	1534	1534	1534
FGR ratio, %	-	61.1	62.8	-	62.1	63.7	-	59.6	61.7
O_2 concentration, % Vol	21%/N_2	31.6	30.0	21%/N_2	30.3	28.9	21%/N_2	30.8	29.0
Flue gas flow rate, kmol/s	14.3	9.52	10.0	14.8	10.3	10.8	15.1	10.5	11.1
Flue gas composition at 810 °C, % Vol									
CO_2	15.4	77.4	66.1	14.8	78.1	64.7	14.7	75.1	60.5
H_2O	12.7	19.1	30.4	12.8	18.4	31.8	14.9	21.4	36.1
NO_2 (ppmv)	27.0	1.51	1.40	29.1	1.29	1.19	27.2	1.40	1.27
SO_2 (ppmv)	0.12	0.18	0.16	0.12	0.18	0.15	0.12	0.18	0.14
CO (ppmv)	0.08	0.36	0.30	0.07	0.36	0.29	0.08	0.35	0.28
Ash flow rate, kg/s	62.5	80.2	80.2	44.2	56.6	56.6	50.8	65.0	65.0
Ash composition, % mass									
$CaCO_3$	0	50	50	0	49.7	49.7	0	49.6	49.6
CaO	35.8	0	0	35.6	0	0	35.5	0	0
$CaSO_4$	13.4	10.5	10.5	14.0	10.9	10.9	14.0	10.9	10.9
Fe_2O_3	3.0	2.3	2.3	3.1	2.4	2.4	3.1	2.4	2.4
Wood ash	-	-	-	0.15	0.11	0.11	0.5	0.4	0.4
Recycled flue gas composition, % Vol									
CO_2	-	95.6	76.5	-	95.8	73.8	-	95.6	70.3
H_2O	-	0	19.5	-	0	22.3	-	0	25.7
Other	-	4.4	4	-	4.2	3.9	-	4.4	4

Table 7: Physical properties of flue gas and oxidizer for EOS and its blends.

	Air EOS	OF EOS		Air EOS/WC	OF EOS/WC		Air EOS/SCE	OF EOS/SCE		Air EOS/WC/SCE	OF EOS/WC/SCE	
FGR option	-	Dry	Wet	-	Dry	Wet	-	Dry	Wet	-	Dry	Wet
Temperature (ºC)	1546	1546	1546	1598	1598	1598	1461	1461	1461	1534	1534	1534
Flue gas heat capacity (kJ/kmol.K)	37.54	52.09	50.27	37.67	51.78	49.83	37.75	52.02	50.57	37.81	51.73	49.85
Flue gas heat capacity (kJ/kg.K)	1.28	1.34	1.43	1.30	1.35	1.45	1.28	1.34	1.41	1.3	1.36	1.45
Flue gas mass flow rate (kg/s)	435	399	381	454	428	406	419	368	356	438	400	381
Flue gas density (kg/m^3)	0.32	0,43	0,39	0,32	0,42	0,38	0,32	0,43	0,40	0,32	0,42	0,38
Oxidant heat capacity (kJ/kmol.K)	-	39.9	38.6	-	40.1	38.5	-	39.7	38.7	-	39.9	38.4
Oxidant heat capacity (kJ/kg.K)	-	0.991	1.073	-	0.992	1.084	-	0.990	1.055	-	0.991	1.081
Oxidant mass flow rate (kg/s)	-	360	342	-	377	354	-	329	318	-	351	332
Oxidant density (kg/m^3)	-	1,031	0,919	-	1,030	0,894	-	1,032	0,941	-	1,031	0,909

Sensitivity analysis

The effect of combustion temperature on the gas concentrations (or emissions) of CO, SO_2 and NO_2 on a ppm volume basis is shown in *Figure 10abc*. Each simulated case shows similar behaviour in the given temperature range (between 750 and 900°C). As the combustion temperature is increased, the concentration of selected gaseous emissions is raised in the flue gas composition. SO_2 and CO emissions are drastically increased after 840°C for each blended fuel types and NO_2 concentration is increased linearly as the temperature is raised. However, there is a sharp decrease between 840 and 850°C for each blended fuels. The highest calculated NO_2 emission is at 840°C for EOS/SCE blend. *Figure 10d*, shows the change in CO_2 concentration on a mol % basis. There is no remarkable change in CO_2 emissions until 840°C for each blended fuel types however, a rapid increase in CO_2 emissions is observed at 840°C after that no considerable temperature effect is detected on CO_2 gaseous emissions.

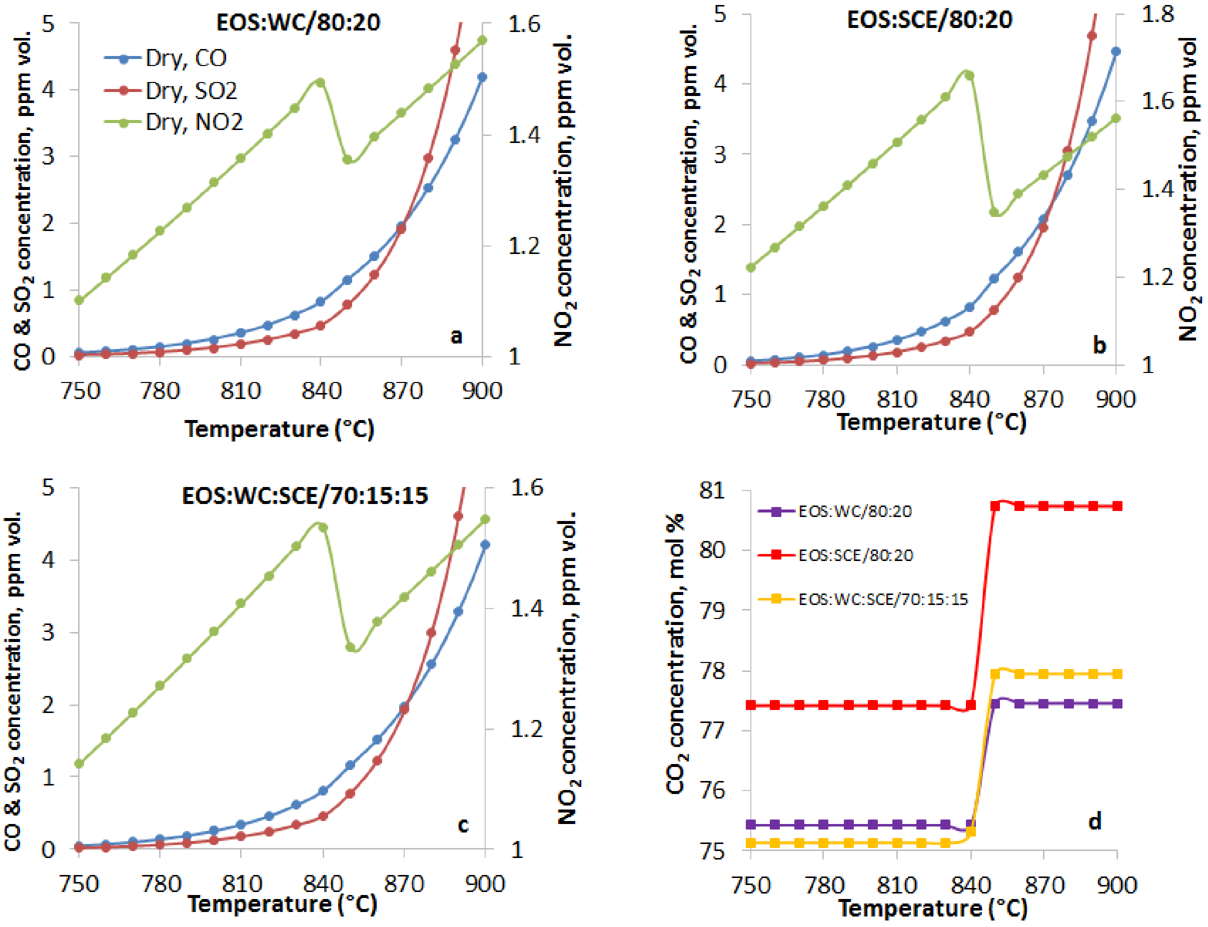

Figure 10: Temperature effect on gas emissions for EOS:WC (a), EOS:SCE (b), EOS:WC:SCE (c) and CO_2 concentrations for fuel blends (d).

The effect of WC ratio on gaseous emissions and ash flow rate

The model of OF and air combustion have been simulated for different blend ratios of EOS and WC in order to observe the effects of changing WC and SCE ratio on the ash flow rate and flue gas compositions. The influence of changing WC ratio on NO_x, SO_x, CO_2 emissions and ash flow rate is shown in *Figure 11*. As it can be seen from the *Figure 11abd*, NO_x, SO_x, CO_2 concentrations decrease in both atmospheres as the WC ratio is increased since sulphur content was rather less in WC compared to EOS and similarly, due to the less nitrogen content of WC compared to EOS. Due to the decreasing mineral content with the increase of WC in the mixture, there are lower CO_2 emissions in both atmospheres.

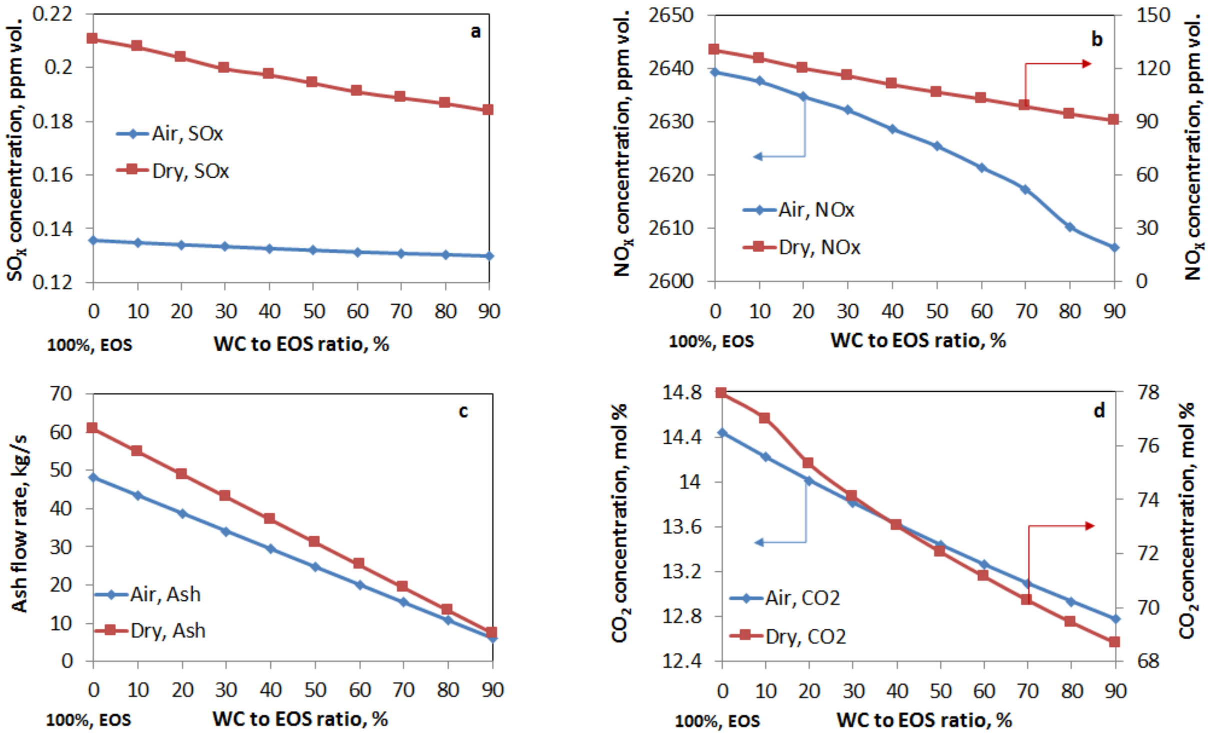

Figure 11: Gas emissions and ash flow rate versus ratio of WC to EOS.

SO_x and NO_x concentrations (Fig. 11ab) are higher in OF combustion due to the lower total flue gas flow rate and the recycling of SO_x and NO_x in the flue gas back to the combustor. Furthermore, $CaCO_3$ is not decomposed completely in OF and SO_2 can not be totally bonded to form $CaSO_4$ thus leading to increase on SO_x concentration compared to air atmosphere. However, $CaCO_3$ is decomposed completely in air atmosphere and all CaO formed can react with SO_2 to produce $CaSO_4$ and hence resulting in lower SO_x concentration in air.

The effect of WC on final ash residue can clearly be seen from *Figure 11c*. Ash flow rate in the product stream of combustor is decreased as WC ratio is increased in the mixture. With respect to decreasing trend on ash flow rate, the ash formation in EOS:WC/80:20 blend decreases 9.3 kg/s and 11.8 kg/s compared to individual EOS fuel in air and OF atmosphere, respectively. The ash flow rate in OF is greater than air due to the higher CO_2 partial pressure in OF atmosphere that avoids complete carbonate decomposition and hence causing a raise in ash content.

The effect of SCE ratio on gas emissions and ash flow rate

Figure 12, presents the influence of SCE ratio on NO_x, SO_x, CO_2 emissions and ash flow rate. SO_x flow rate in the flue gas (*Fig. 12a*) decrease in air and OF atmospheres as the SCE ratio is increased due to the less sulphur content of organic part in SCE. As can be seen in figure, SO_x flow rates are very similar in both atmospheres for the specified SCE to EOS ratio. NO_x concentration (*Fig. 12b*) is increased slightly for 90:10 (EOS/SCE) blend however further increase of SCE ratio results in decrease of NO_x concentration in air and OF atmospheres owing to less nitrogen content of SCE.

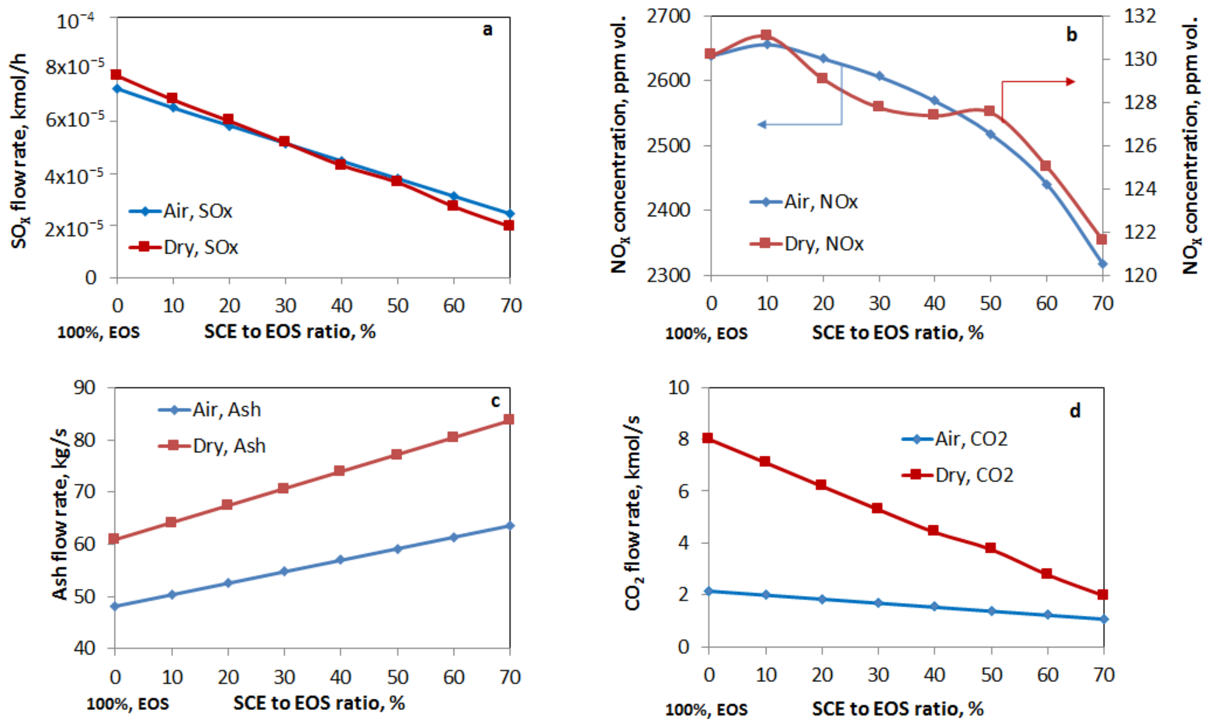

Figure 12: Gas emissions and ash flow rate versus ratio of SCE to EOS.

Nevertheless, NO_x concentration remains almost constant for the ratios of 30, 40 and 50% of SCE. NO_x concentration is considerably higher in air compared to OF due to the high nitrogen content in oxidizer. The ash flow rate (*Fig. 12c*) is increased in both atmospheres as the SCE to EOS ratio in the blend is raised, since mineral content of SCE is greater than the amount of mineral in EOS. In addition, ash flow rate is greater in OF due to the influence of high CO_2 partial pressure. *Figure 12d,* shows the change of CO_2 emissions. CO_2 emission decreases as the SCE ratio is increased in both atmosphere and this drop is more visible in OF due to the higher partial pressure of CO_2 which avoids the decomposition of $CaCO_3$.

5. CONCLUSIONS

The conclusions based on the experimental and modeling studies can be listed as follows:

Experimental

- According to TA results the blended fuels reflect a similar trend in mass loss with the individual fuels, depending mainly on their ratios in the blend and showing no significant synergetic effects.
- Co-combustion of EOS with PSD enhances the combustion process by lowering the characteristic (onset, offset and peak) temperatures of oxidation stage and increasing the reactivity due to the high volatile and oxygen content of PSD which can be considered as a positive effect on combustion.
- However, co-combustion of EOS with SCE leads to higher peak (maximum reactivity) temperatures compared to EOS and EOS/PSD, due to the volatile-free organic part (only fixed carbon in SCE) and high minerals content of the fuel which has a negative effect on the combustion process.
- The blends of three fuels (EOS:PSD:SCE) show rather similar characteristic temperatures with only EOS showing that this can be a good alternative to EOS firing.
- The calculated conversion-dependent activation energies are higher for EOS:SCE mixture indicating to the increased role of reactions in mineral part. Also, oxidation stage proceeds at higher E_A values compared to EOS and EOS:PSD due to the volatile-free organics and high minerals content of SCE. On the contrary, blending of EOS with PSD (80:20) leads to a drop in the activation energy compared to EOS only indicating to possible higher reaction rates at the same temperature.
- Under OF conditions for EOS, SCE and their blends, the mineral part related decomposition of carbonates takes place in two steps and $CaCO_3$ is decomposed at higher temperatures compared to model air atmosphere due to higher partial pressure of CO_2. However, EOS/PSD blends show reduced peak temperatures of carbonates decomposition compared to EOS only. This can be explained by lower mineral content of this fuel mix which leads to lower mineral CO_2 content and, respectively, CO_2 partial pressure in the test atmosphere and should not affect in the real process.

Another reason can also be the catalytic effect of alkali compounds in PSD ash. Thus, lower operating temperatures should be considered to avoid the enhanced release of mineral CO_2 and endothermic effect of carbonate decomposition, especially, in air combustion.

Modeling

- It is possible to reach similar combustion temperature levels for all the simulated OF cases as in air combustion case by increasing O_2 concentration to almost 30%O_2.
- EOS:SCE blend gives lower temperature values due to the high content of mineral matter and related endothermic effects as well as slightly higher flue gas heat capacity calculated for the ideal gas mix. Thus, co-combustion of EOS with SCE affects the heat balance negatively without any addition of the third biomass fuel.
- OF combustion leads to remarkably higher ash flow rates compared to air combustion owing to the behaviour of carbonates in EOS and SCE. However, ash flow rate is decreased as WC ratio to EOS is increased in the feed mixture due to its considerably low ash content.
- NO_x, SO_x, concentrations decrease in both atmospheres as the WC and SCE to EOS ratio is increased since sulphur and nitrogen content in WC and SCE is low compared to EOS. However, NO_x and SO_x concentrations are higher in OF than in air combustion due to the lower total flue gas flow rate and the effect of RFG. Moreover, almost 80% of $CaCO_3$ stays undecomposed in OF, therefore part of SO_2 is not bound to form $CaSO_4$ leading to an increase in SO_x concentration.
- Sensitivity analysis for EOS, SCE and WC blends shows that the emissions of CO, SO_2, NO_2 and CO_2 increase if the combustion temperature is increased. Temperatures between 800 and 840°C can be suggested as the optimum operating temperatures.

As a consequence, on the basis of both experimental and modeling work, co-combustion of EOS with biomass and SCE in OF combustion can be a promising solution for the reduction of CO_2 emissions from Estonian power sector and also for the complete utilization of the heating value of SCE as the endothermic effect of decomposition of $CaCO_3$ (for both OS and SC) can be diminished and sensible heat from SCE can positively affect energy balance of the overall process.

RÉSUMÉ

The conventional combustion of local fuel oil shale (OS) provides a relatively high degree of energy security in Estonia. However, existing technologies of OS combustion and retorting create serious environmental problems due to the excessive usage of OS which leads to high carbon footprint and huge amounts of solid waste – semi-coke (SC) and ash. In this respect, implication of modern technologies by increasing the share of biomass in energy production and focusing on the utilization of solid wastes from OS retorting with partial fuel switching from 100% OS to co-combustion of OS with biomass and SC can give enhanced flexibility to Estonia's OS capacity. These applications can also be brought up to date with the OF combustion technology for more sustainable and environmentally friendly usage of OS.

In the current work, thermal behaviour of Estonian OS (EOS) and its SC (SCE), pine saw dust (PSD) and their blends (EOS with SCE and PSD) were studied by thermal analysis methods. Experiments were carried out comparatively under model OF and air combustion conditions. The effect of additive SC and PSD on the kinetics of different combustion stages under air combustion conditions was discussed. In addition, different co-firing cases were simulated using the ASPEN PLUS V8.6 software tool. OF combustion cases have been simulated with dry and wet FGR strategies by controlling the O_2 percentage in flue gas on the basis of maintaining similar temperatures (of gas-solid mixture) at the outlet of combustion reactor similar to the temperature at air combustion. The main target was to evaluate the effects of blending EOS with other fuels regarding the operation conditions of air and OF combustion and to calculate the specific boiler temperatures with the same thermal input. The composition of flue gas was estimated for different cases from mass–energy balance and chemical equilibrium calculations. For this purpose, simulations were built up for a wide range of mixing ratios of SC and different types of biomass to evaluate specific gaseous emissions such as SO_x, NO_x as well as CO_2 and ash flows. Finally, the temperature effect on gaseous emissions (CO, SO_2, NO, NO_2 and CO_2) in air and OF combustion conditions was studied by sensitivity analysis.

According to the experiment and process simulation results, the co-firing of EOS with PSD lowers the ignition temperature and enhances combustion, due to high volatile content of PSD. In contrary, higher maximum reactivity temperatures were registered for EOS/SCE blends compared to EOS and EOS/PSD. There is no evidence of any significant synergetic effects between either PSD or SCE during the co-combustion with EOS as the mass loss of the blends reflects the behaviour of the individual components, depending on the blending ratios. However, decomposition temperatures of $MgCO_3$ and $CaCO_3$ are shifted to lower temperatures for blended samples, especially, for EOS/PSD. Thus, to avoid the release of mineral CO_2 and endothermic effect of carbonate decomposition, lower operating temperatures should be considered in the case of blends.

For all the simulated OF cases, it is possible to reach similar temperature levels as in air combustion case by increasing O_2 concentration to almost 30%O_2 levels. All fuel blends of EOS except for EOS/SCE have reached higher temperature values during co-combustion compared to combustion of solely EOS. Thus, OF co-combustion of EOS with different types of biomass fuels (WC, WP, PSD) shows that these fuel blends can be a good alternative to merely EOS combustion, providing similar boiler temperatures. Both dry and wet FGR can be applied depending on the fuel quality and moisture content of the biomass and SC. Due to the behaviour of carbonates in OS and SC, there is a notably higher ash flow rate in OF combustion cases. The high moisture content of biomass reduces the boiler temperature, making it more difficult to sustain the similar temperature level with optimum FGR ratio.

The low heating value and high carbonate content of SC brings along endothermic decomposition of carbonates which can affect the heat balance negatively, if the moisture content of SC is high. However, the endothermic effect of decomposition of $CaCO_3$ (for both OS and SC) can be diminished in OF combustion and sensible heat from SC can positively affect energy balance of the system. Consequently, firing of OS with biomass and SC in OF process can give an effective solution for the reduction of CO_2 emissions and also for the utilization of the residual heating value of SC.

RESÜMEE

Põlevkivi (PK) põletamine kindlustab Eestile vajaliku energiajulgeoleku. Samas tekitavad olemasolevad põletamis- ja utmistehnoloogiad PK suuremahulise kasutamise tõttu tõsiseid keskkonnaprobleeme – suurt süsiniku jalajälge ja tohutuid koguseid tahkheitmeid tuha ning poolkoksi näol. Sellest seisukohast lähtudes oleks vajalik rakendada nii uusi tehnoloogiaid kui suurendada biomassi osatähtsust energiatootmises, pöörates tähelepanu utmisel tekkivate tahkjäätmete kasutusele ning minna üle ainult PK põletamiselt selle koospõletamisele biomassi ja poolkoksiga. Selline lahendus pakuks paindlikumaid võimalusi Eesti põlevkivi-ressursi kasutamiseks. Põletustehnoloogiat saaks tänapäevastada nn. hapnikuspõletamise rakendamisega, mis aitaks samuti kaasa põlevkivi jätkusuutlikumale ning keskkonna-sõbralikumale kasutamisele.

Käesolevas töös uuriti termilise analüüsi meetodeid rakendades Eesti põlevkivi, selle poolkoksi (PKO), männipuidu saepuru (SP) ning nende segude termilist käitumist kuumutamisel õhus-põletamise ja hapnikuspõletamise mudeltingimustel. PKO ja SP lisamise mõju põlemisprotsessi eri staadiumide kineetikale uuriti õhus-põletamise tingimustel. Lisaks simuleeriti mitmeid erinevaid koospõletamise variante ASPEN PLUS V8.6 tarkvara kasutamisega. Hapnikuspõletamise protsessi modelleeriti nii kuiva kui märja retsükli rakendamisega, kontrollides hapniku sisaldust gaasifaasis nii, et gaasiliste ja tahkete produktide temperatuur reaktorist väljumisel oleks sama, mis õhus-põletamise puhul. Peamiseks eesmärgiks oli hinnata koospõletamise mõju protsessi parameetritele nii õhus- kui hapnikuspõletamisel ja määrata temperatuurirežiimid sama soojuskoormuse juures. Massi ja energiabilansside ning tasakaaluarvutuste teel leiti suitsugaaside koostised erinevatel valitud juhtudel. Selleks varieeriti PK, PKO ja biomassi segude koostisi laiades piirides, mis võimaldas koostatud mudelite abil arvutada spetsiifiliste gaasifaasi komponentide (CO, SO_2, NO, NO_2 ja CO_2) emissioonid ning tuhavood ja teha kindlaks põletamistemperatuuri mõju nendele emissioonidele mõlema põletustehnoloogia puhul.

Vastavalt eksperimentide ja mudelarvutuste tulemustele alandab PK põletamine koos saepuruga süttimistemperatuuri ning kiirendab põlemisprotsessi tingituna SP kõrgest lendainete sisaldusest. PK ja PKO segude korral fikseeriti aga märksa kõrgemad maksimaalse oksüdatsioonikiiruse temperatuurid võrreldes PK ja PK/SP segudega. Ei leitud

märkimisväärseid sünergeetilisi efekte SP ja PKO koospõletamisel põlevkiviga – massikaod kuumutamisel peegeldasid erinevate komponentide iseloomulikku käitumist vastavuses nende sisaldusega kütusesegudes. Siiski nihkusid $MgCO_3$ ja $CaCO_3$ lagunemise algustemperatuurid mõnevõrra madalamate väärtuste suunas, seda eriti PK/SP segude korral. Seega tuleks karbonaatse CO_2 emissiooni kasvu ja karbonaatide lagunemise endoefekti negatiivse mõju vältimiseks kasutada segude puhul madalamat põletamistemperatuuri.

Kõikide simuleeritud hapnikuspõletamise juhtude korral oli võimalik jõuda samadele temperatuuriväärtustele nagu õhus-põletamisel hapniku sisalduse suurendamisega oksüdeerivas gaasis 30% tasemeni. Koospõletamisel näitasid kõik kütusesegud v.a. PK/PKO kõrgemaid temperatuure võrreldes ainult PK põletamisega. Seega saab järeldada, et PK koospõletamine biomassiga (puidugraanulid, pelletid, SP) on heaks alternatiiviks PK põletamisele, kindlustades praktiliselt sama temperatuuri boileris. Lähtuvalt kütuse kvaliteedist ja biomassi ning PKO niiskussisaldusest saab rakendada nii kuiva kui märga retsüklit. Kõrge niiskussisaldus biomassis võib alandada boileri temperatuuri ja teha raskemaks sama temperatuurirežiimi säilitamise optimaalsete FGR väärtuste juures. Karbonaatide madalama lagunemisastme tõttu on hapnikuspõletamise korral tuhavoog märgatavalt suurem.

PKO madal kütteväärtus ning kõrge karbonaatide sisaldus toob kaasa nende endotermilise lagunemise, mis mõjutab negatiivselt protsessi soojusbilanssi, eriti kui ka niiskussisaldus poolkoksis on kõrge. Seda endotermilist efekti (nii PKO kui PK puhul) saab vähendada hapnikuspõletamise rakendamisega, mis võimaldaks ära kasutada PKO jääk-kütteväärtuse positiivse mõju energiabilansile.

Seega on PK põletamine koos biomassi ja poolkoksiga hapnikuspõletamise tingimustel efektiivseks lahenduseks CO_2 emissiooni vähendamiseks ning poolkoksi jääk-kütteväärtuse ärakasutamiseks.

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