

Oxidation Kinetics of Oil Shale under Oxyfuel Conditions

C. R. Yörük, T. Meriste, [A. Trikkel](#), R. Kuusik
Tallinn University of Technology, Estonia
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Background

- Power production in Estonia is predominantly based on combustion of a local fossil fuel – Estonian oil shale (OS).
 - 90% of electricity production
 - 66% of primary energy
- OS is a specific fuel due to its low calorific value, high content of carbonaceous mineral matter, so, its combustion is related to formation CO_2 also from carbonates (CaCO_3 , MgCO_3).



Estonian OS:

LHV:	8...9 MJ/kg
H/C mole ratio:	~1.5
Mineral part:	65...70%
carbonates:	~50%
A^d :	45...47%
$\text{CO}_2^{d,M}$:	16...19%
S^d :	~1.5%

Background

Parameter	Coal	Estonian OS	Jordanian OS
W, %	5–13	10–12	10–12
LHV, MJ/kg	20–28	8–9	3.6–6
A ^d , %	5–25	43–47	63–65
CO ₂ ^{M,d} , %		16–19	19
S ^d , %	0.5–3	1.5–1.8	2.5



1 ton of Estonian OS
gives



125 kg of shale oil
35 Nm³ semi-coke gas
180 kg of CO₂
+ SO_x, NO_x, VOC, PM



850 kWh electricity
870 kg of CO₂
+ SO_x, NO_x, VOC, PM



450 kg of ash

Background

How to provide economically viable energy supply with low CO₂ emissions having at the same time continuous large share of fossil fuels in the energy balance?

No one absolute solution...

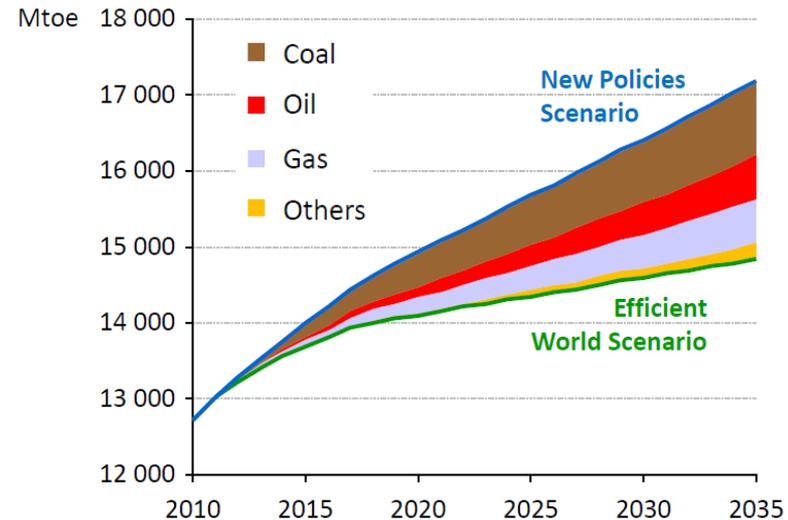
In Estonia pulverized firing is being replaced by CFBC technology:

PF: $K(\text{CO}_2) = \sim 0.97$

CFBC: $K(\text{CO}_2) = \sim 0.68$

One technical option for further reduction of CO₂ emissions can be oxyfuel combustion.

Total primary energy demand



Source: OECD/IEA, WEO 2012

Estonia:

OS consumption rate 18.7 mln t/y

80% for electricity production

18% for shale oil production

CO₂ emissions:

18.5 mln t/y from energy sector

87% from all GHG emissions

No CCS used up to now

Aim of the research

- Oil shale and coal differ notably in their organic and mineral composition.
- Estonian OS has never been studied as a fuel in oxyfuel combustion.
- **So, the aim of this research, was to study the fundamentals of oxyfuel combustion of Estonian OS:**
 - By means of thermal analysis and FTIR methods, several characteristics of the process were clarified and kinetic parameters of oxidation stage were calculated.
 - Comparison was given
 - a) with selected coal samples
 - b) with air combustion conditions

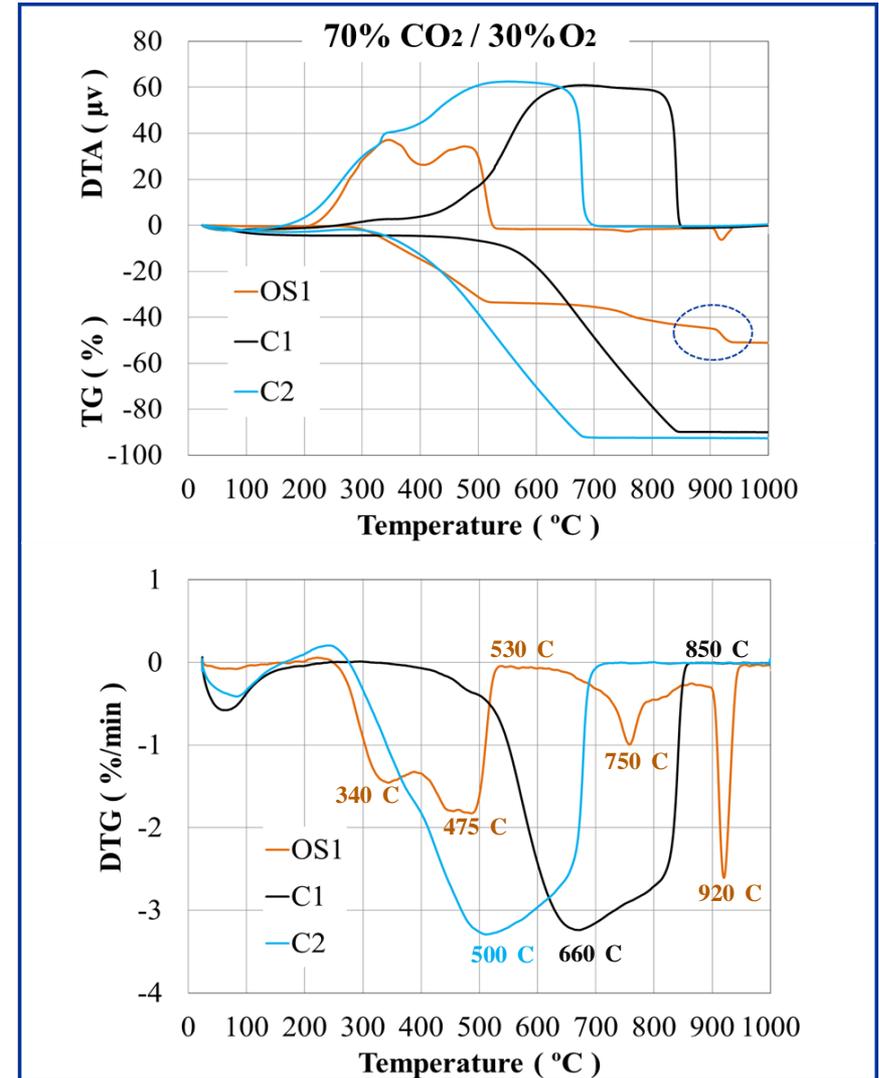
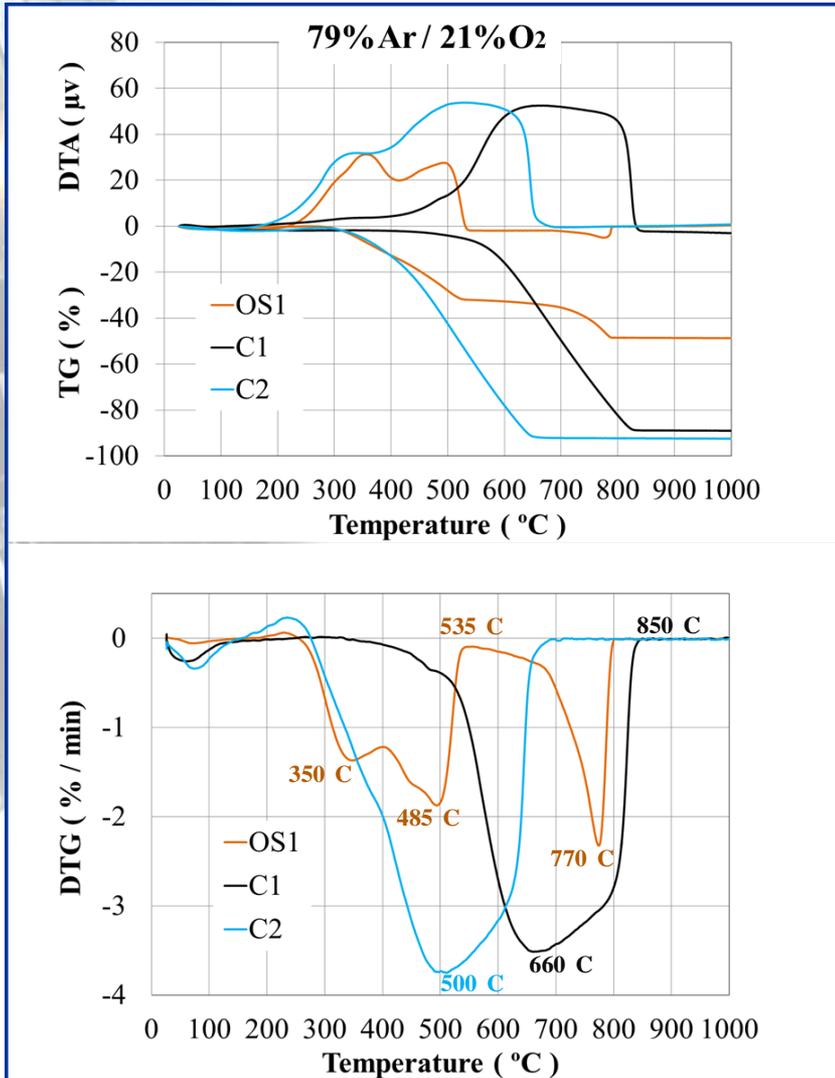


Materials and methods

- OS samples (**OS1** and OS2); one anthracite coal (**C1**) and conventional coal (**C2**) sample were tested.
- Fuel samples were crushed, dried and ground to pass the 200 μm sieve, the mean sample was used in most TG experiments.
- For kinetic analysis tests a narrower fraction 71...100 μm was selected.
- The experiments were carried out with a Setaram Setsys Evo 1750 thermoanalyzer coupled to a Nicolet 380 FTIR spectrometer (non-isothermal heating up to 1000°C or 1100°C at 10 K min⁻¹).
- Standard 100 μL Pt crucibles were used, the mass of samples was 20 \pm 1 mg.
- **Gas composition** was **79%Ar / 21%O₂** (to model air) and **70%CO₂ / 30%O₂** (CO₂ / 21...35% O₂) for oxyfuel conditions. Gas flow rate 30 mL min⁻¹.

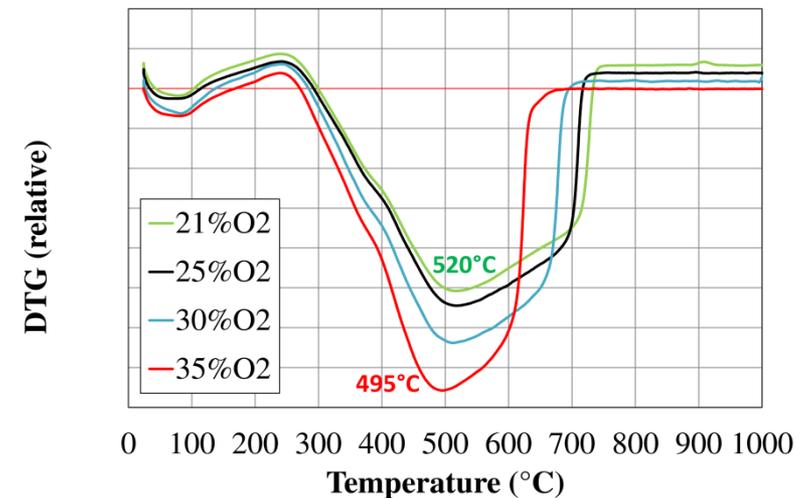
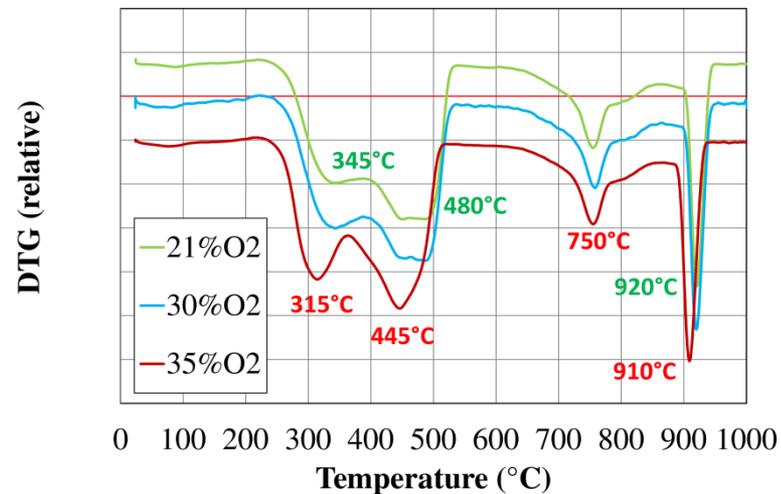
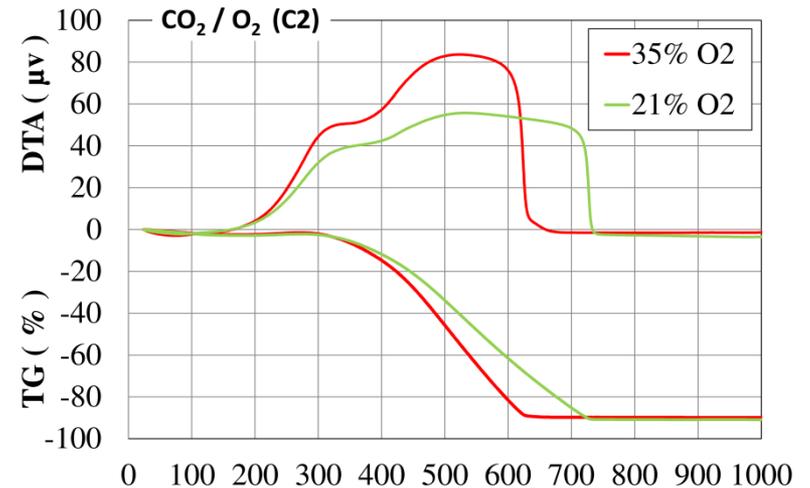
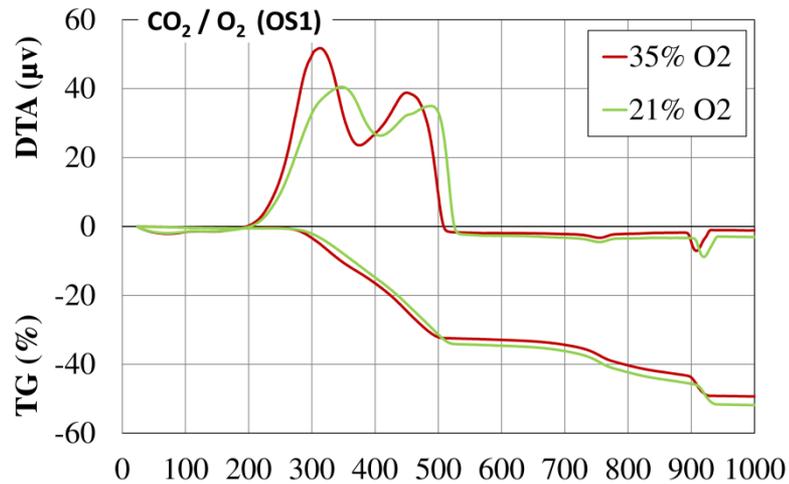
	OS1	OS2	C1	C2
HHV ^d , MJ/kg	11.86	13.64	30.39	30.22
Content, %mass				
Ash ^d	49.3	45.6	8.9	8.1
Moisture W	0.70	0.70	2.1	2.7
Elements				
C ^d	30.4	35.0	81.8	73.7
H ^d	3.0	3.6	1.5	4.2
N ^d	0.1	0.1	0.6	2.0
S ^d	1.63	1.87	0.25	0.36
TC	31.5	36.4	87.0	75.8
TIC / CO ₂ ^M from TIC	4.55 / 16.7	4.35 / 16.0	~0	~0

Results: Comparison of samples and conditions



Thermal analysis curves of the samples in Ar/O₂ (left) and CO₂/O₂ (right)

Results: Effect of O₂ concentration



Thermal analysis curves of OS1 (left) and C2 (right) in CO₂/O₂ at different O₂ concentrations

Results: FTIR analysis

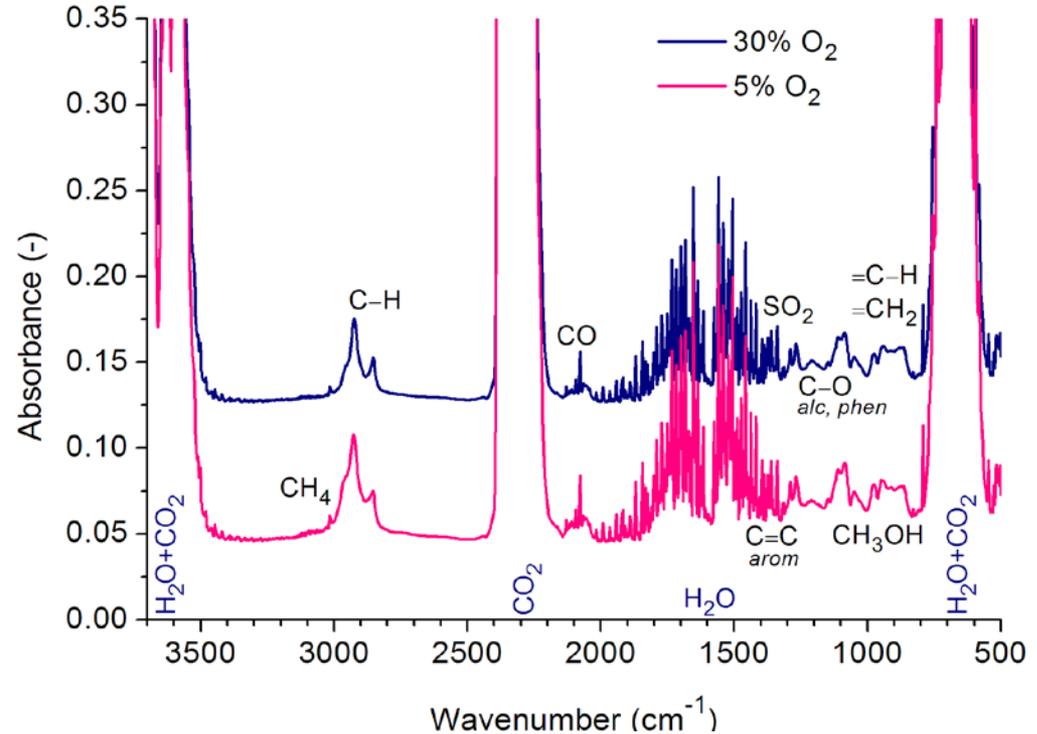
FTIR analysis of the evolved gas mixture is complicated due to huge and partly overlapping CO_2 and H_2O peaks in several regions.

To get better overview, increased heating rate (20 K/min), sample mass and gas flow rate were used and different O_2 concentrations (30...0%) were tested.

Still several important groups, bonds and compounds were identified.

E.g. C–H bond describing saturated hydrocarbons, C–O bond of alcohols and phenols. CH_4 , CO and SO_2 were present under all tested conditions, C=C peaks of aromatics intensified at lower oxygen concentrations.

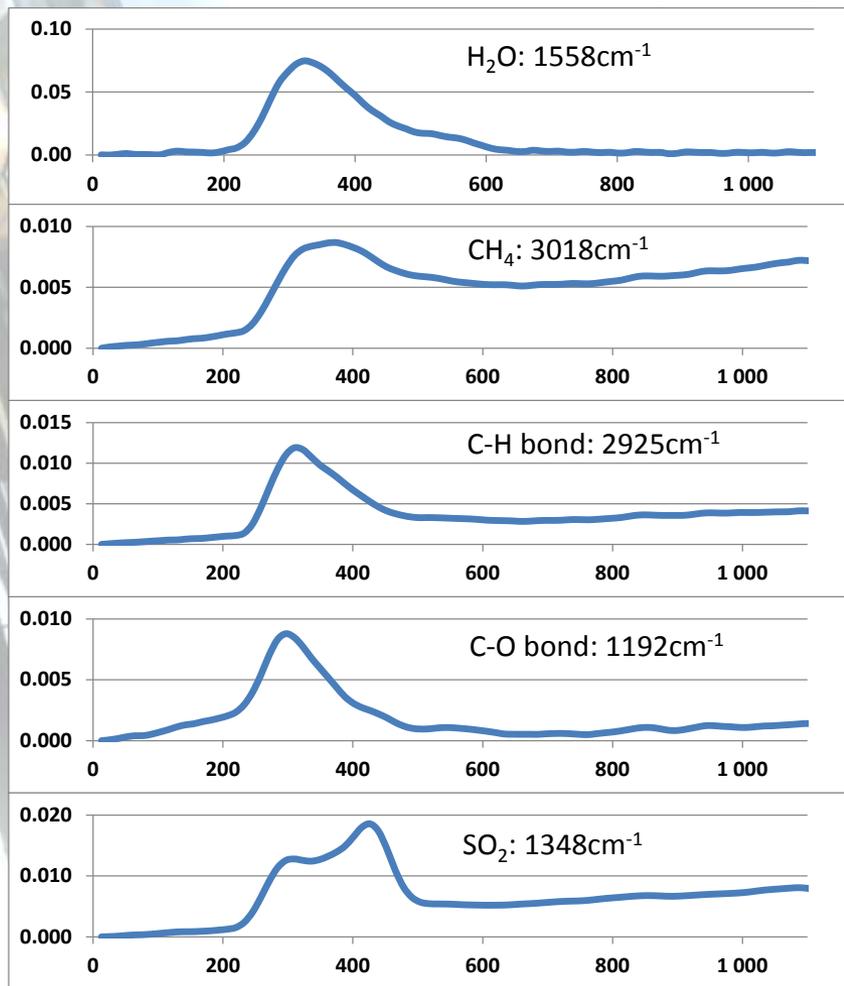
The respective emission profiles were compiled.



FTIR spectra of evolved gases for OS1 at 30% and 5% O_2 content in CO_2 (taken at 440 C)

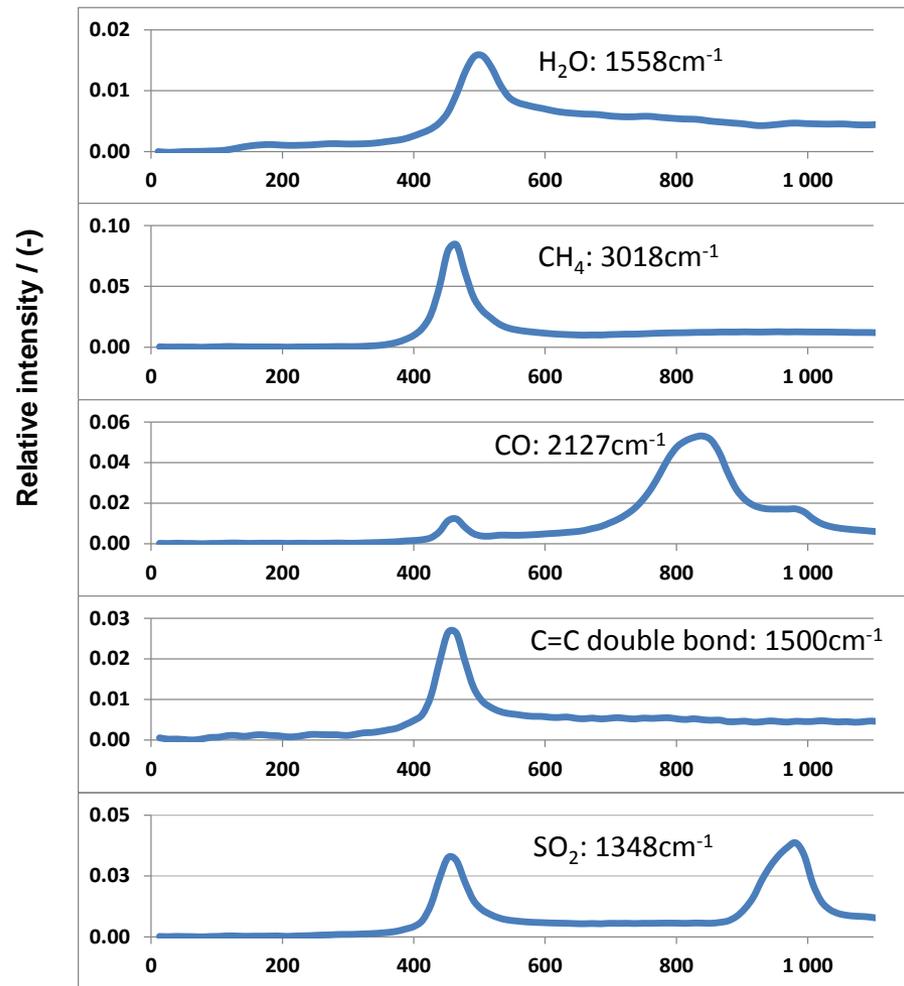
Results: Emission profiles

In CO₂ / 30% O₂



Temperature /°C

In 100% CO₂



Temperature /°C

Emission profiles of selected gas phase compounds and groups

Results: Kinetics

To calculate the conversion-dependent activation energies, a model-free approach, based on differential isoconversional methods was applied.

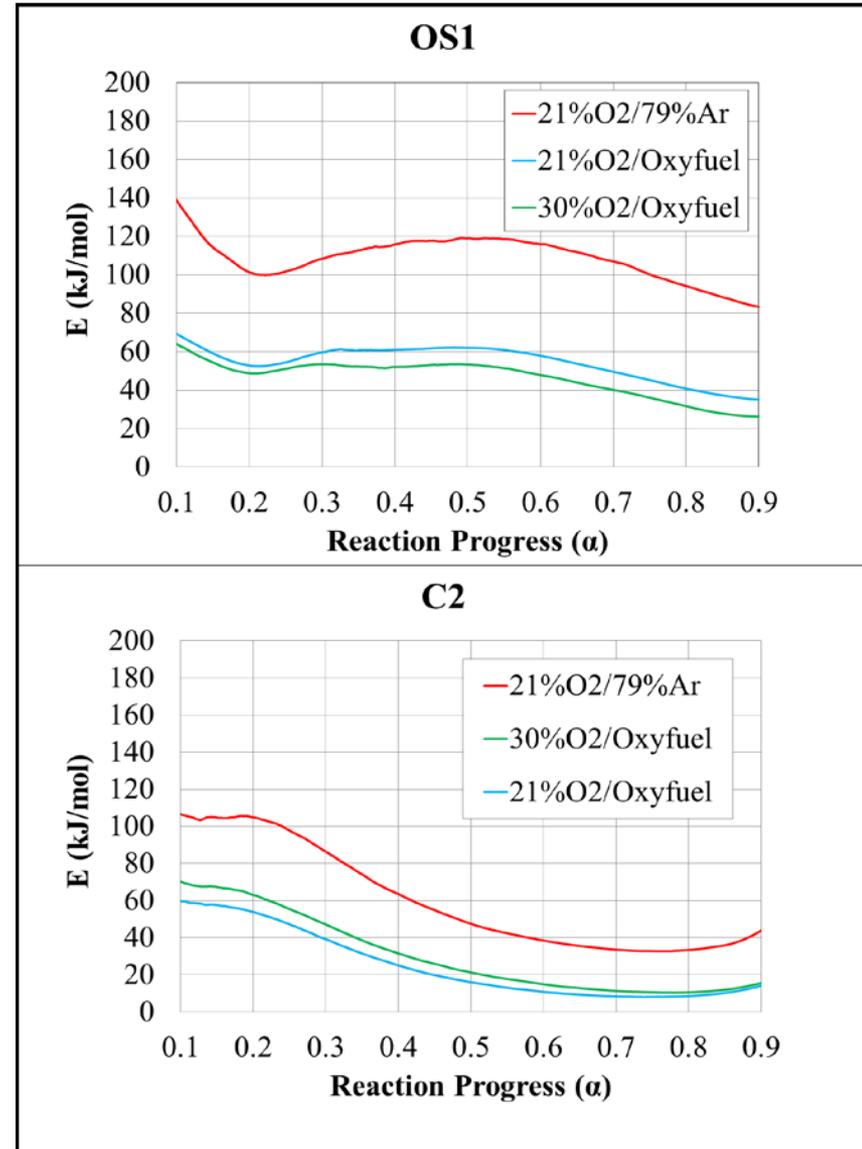
$$\ln \left(\frac{d\alpha}{dt} \right) = \ln \{A(\alpha) f(\alpha)\} - \frac{E(\alpha)}{RT}$$

The calculations were made in Ar / 21%O₂ and CO₂ / 21 or 30% O₂ for the oxidation stage.

The activation energy values for all the samples tested were by 40-50% lower in CO₂/O₂ as compared to Ar/O₂ environment.

The increase in O₂ concentration in oxyfuel atmosphere decreased the apparent activation energy for OS1 sample.

However, there was a slightly opposite effect in the case of C2 sample.



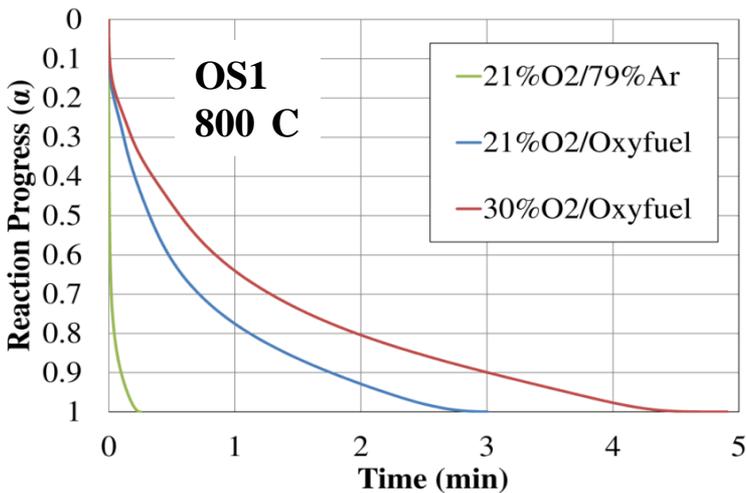
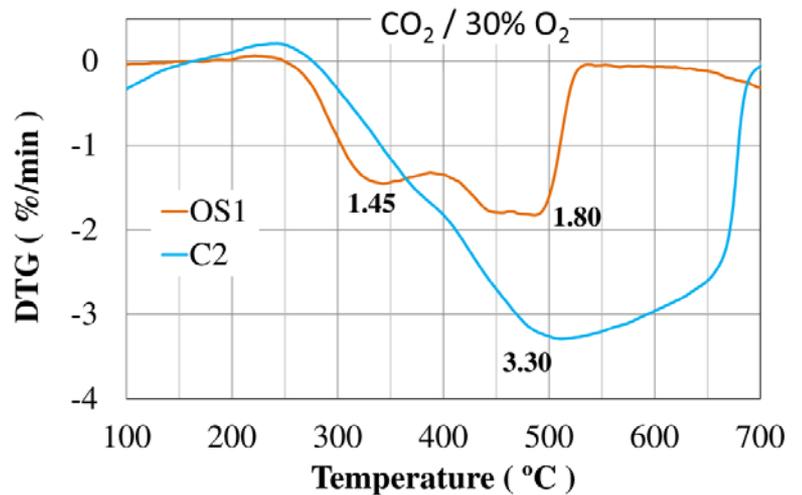
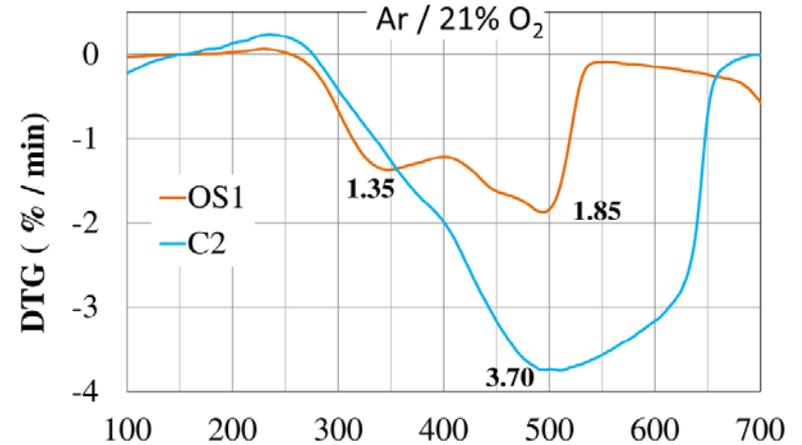
Conversion-dependent activation energy for OS1 and C2

Results: Kinetics

On the basis of activation energies obtained, the isothermal conversion predictions were calculated.

The results show that despite lower activation energy, the oxidation process can last longer in CO_2/O_2 as compared to Ar/O_2 atmosphere.

So, somewhat longer residence time or higher temperatures may be needed in oxyfuel combustion.



Isothermal conversion predictions for OS1

Conversion rate at non-isothermal heating

Results: Kinetics

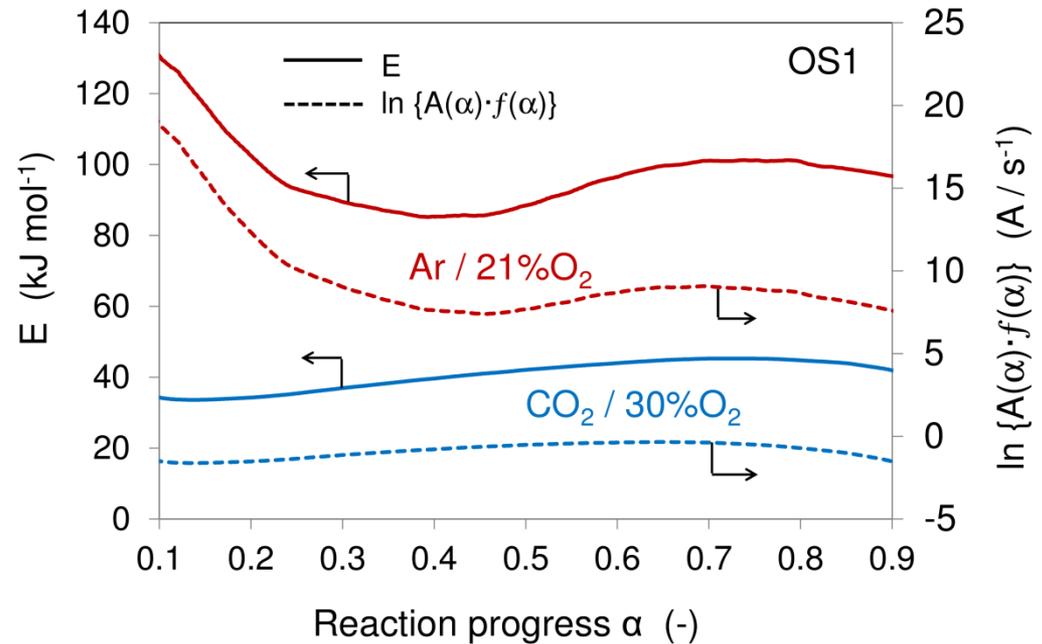
However, lower activation energies should favor process and increase in oxygen concentration should also intensify oxidation.

One reason for these notable differences in process duration can be the kinetic compensation effect (KCE) related to this kind of modeling.

A curves tend to follow **E** curves, but do it on logarithmic scale.

As **A** and **E** affect reaction rate in opposite directions, the differences might not be so visible.

So, isothermal experiments would be also valuable.



Activation energy E and pre-exponential factor A

Conditions	E^{avg} kJ/mol	$\ln \{A(\alpha) \cdot f(\alpha)\}$ A (1/s)	A^{avg} (D3) 1/s ★	τ (800°C) s
CO ₂ / 30% O ₂	78	0.246	0.573	300
CO ₂ / 21% O ₂	81	1.67	2.16	68
Ar / 21% O ₂	145	10.525	24900	2

★ $f(\alpha)$ for $D3$ (Jander diffusion): $\frac{3}{2} (1 - \alpha)^{2/3} [1 - (1 - \alpha)^{1/3}]^{-1}$

Conclusions

- Comparing Ar/O₂ (air) and CO₂/O₂ (oxyfuel) atmospheres, there are no principle differences in the amounts of oxidized matter of the samples tested and in the temperature profiles of the oxidation stage;
 - This enables to assume that there are no fundamental difficulties in applying the oxyfuel combustion to Estonian OS;
- In CO₂/O₂, the decomposition of CaCO₃ is shifted to temperatures above 900 C that can reduce CO₂ emissions from the mineral part of OS and diminish the role of endothermic effect of its decomposition on the heat balance at oxyfuel combustion;
- Combustion reactivity of OS can be notably affected by changing oxygen concentration. At that, CaCO₃ decomposition temperatures stay still at around 900 C;
- Combined TG–FTIR analysis enables to determine a number of gaseous compounds evolved in the process, however, it is sophisticated due to huge and overlapping CO₂ and H₂O peaks;

Conclusions

- In CO₂/O₂ atmosphere, the oxidation stage of OS and tested coal samples proceeded with lower activation energies comparing with Ar/O₂;
- Isothermal conversion predictions calculated from non-isothermal data showed that despite of lower activation energy, oxidation in CO₂/O₂ can last somewhat longer as compared to Ar/O₂ atmosphere;
 - One reason for this can be related to KCE specific to the iso-conversional model used, so, these predictions should be taken with certain caution;
- **The results of the first experiments allow to conclude that oxyfuel combustion can be effectively applied to Estonian Oil Shale for further reduction of CO₂ emissions in Estonian energy sector.**



**Thank you for your
attention!**



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