Research of thermal stability of a solid modified resorcinol - alkylresorcinol - formaldehyde resin

TALLINN UNIVERSITY OF TECHNOLOGY

OIL SHALE COMPETENCE CENTER
VIRUMAA COLLEGE OF TUT

Ana Jurkeviciute, *MSc (Eng)*
Larisa Grigorieva, *PhD*

Tallinn University of Technology, Virumaa College, Oil Shale Competence Center, Kohtla-Järve, Estonia

INTRODUCTION

Resorcinol-formaldehyde resins are widely used in many industrial sectors, such as wood, tire, mechanical rubber articles, etc. When processing oil shale total water-soluble oil shale alkyresorcinols are formed as a by-product.

The synthesis of solids resorcinol-alkylresorcinol-formaldehyde resins modified by styrene, was carried out to enlarge the possibilities of using them. In these resins part of resorcinol is swapped with oil shale alkyresorcinols with boiling point of 270 ºC.

The thermal stability of the resins is an essential parameter of their quality.

The behavior of resins under influence of heat and atmospheric oxygen has an important role in their processing, during use and storage. Information about resin's thermal decomposition and the coking value characterizing its carbonization ability is obtained when heating the resin in inert medium to a high temperature.

EXPERIMENTAL

Method of thermogravimetric analysis (TGA)was used to research thermal processes occurring in the resorcinol-formaldehyde resins of different compositions. The results were obtained using a thermogravimetric analyzer of Mettler Toledo company(Switzerland). Thermal destruction of condensation resins was studied in inert atmosphere of nitrogen and oxidative degradation of the resins – in atmospheric air.

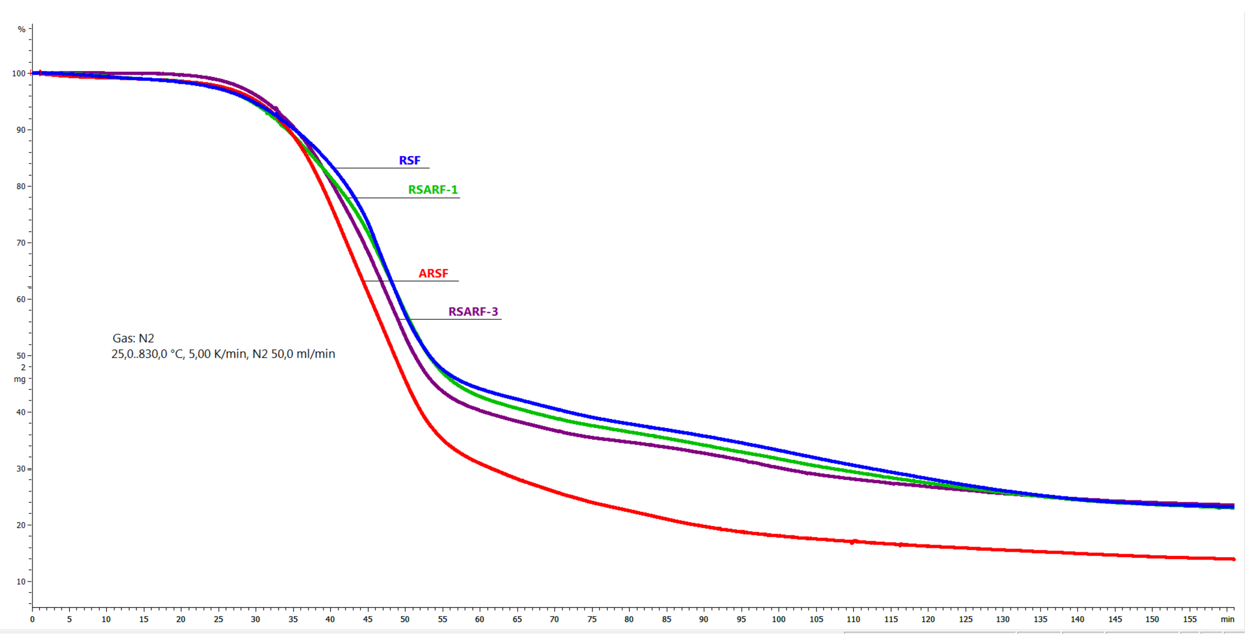
Experimental conditions:

- Dynamic conditions
- Linear temperature rise from 25 °C to 830 °C
- The rate of temperature rise of 5 ° C / min
- Gas flow rate of 50 ml / min
- Alumina crucible

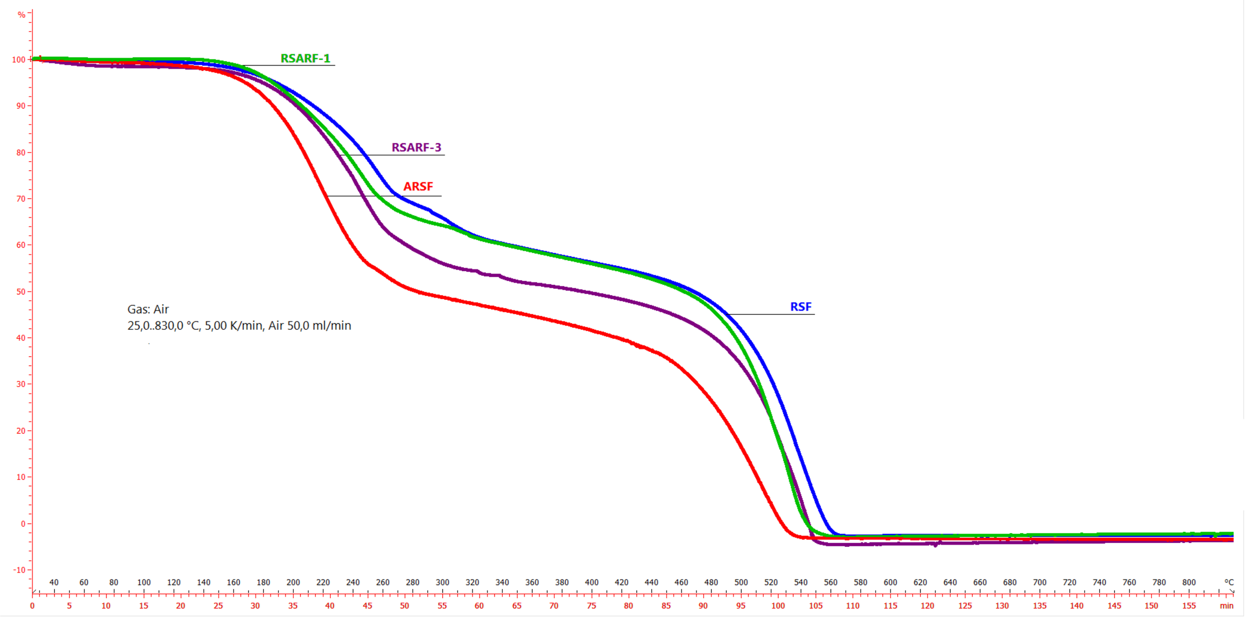
Oil Shale Competence Center
Fuel Technology Research Testing Laboratory
Järveküla tee 75, Kohtla-Järve
Ida-Virumaa, 30322 Estonia
www.pkk.ee

RESULTS

The integral curves of thermogravimetric analysis of resins of different composition in inert atmosphere (Curve 1) and in an oxidizing atmosphere of air (Curve 2) were obtained during research.



Thermogravimetric Curve 1



Thermogravimetric Curve 2

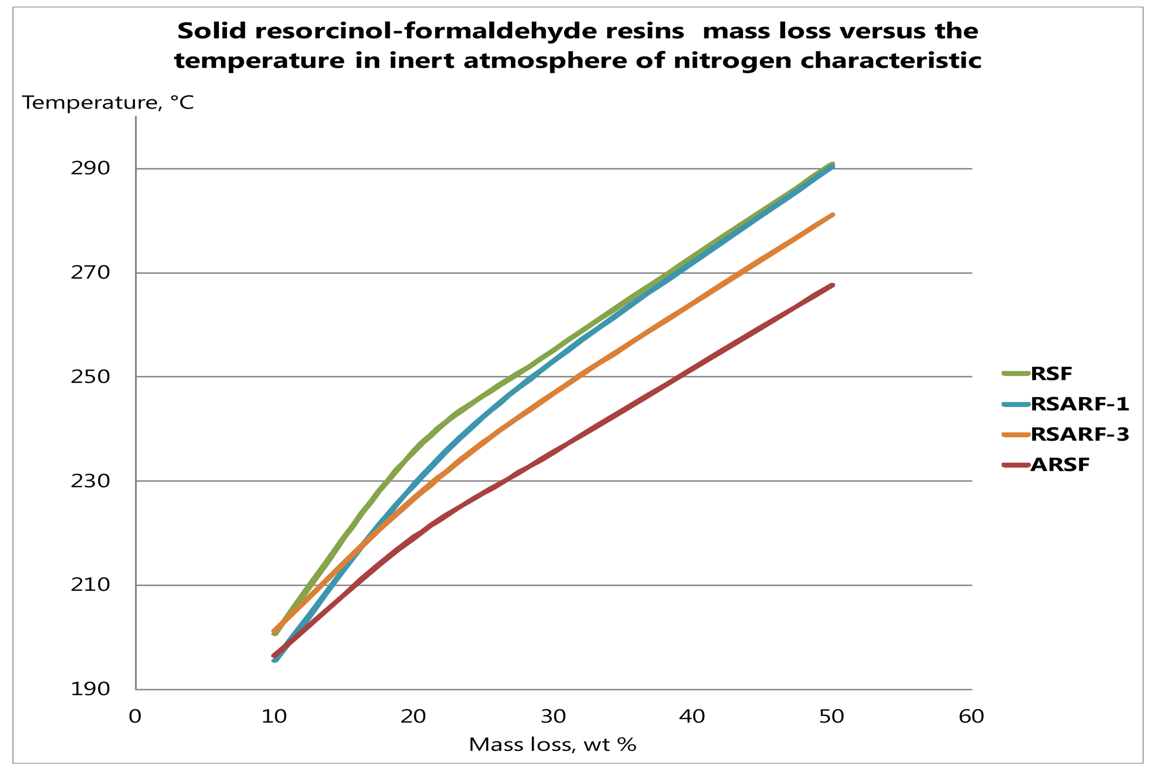
The volatile components content of the resin (ASTM E1868) was determined by TGA in the air at 105°C, ash content (ASTM E1131) - at the temperature of 830°C. The coking values were obtained by heating the resins from 25°C to 830°C in inert atmosphere of nitrogen with a constant heating rate (5°C/min).

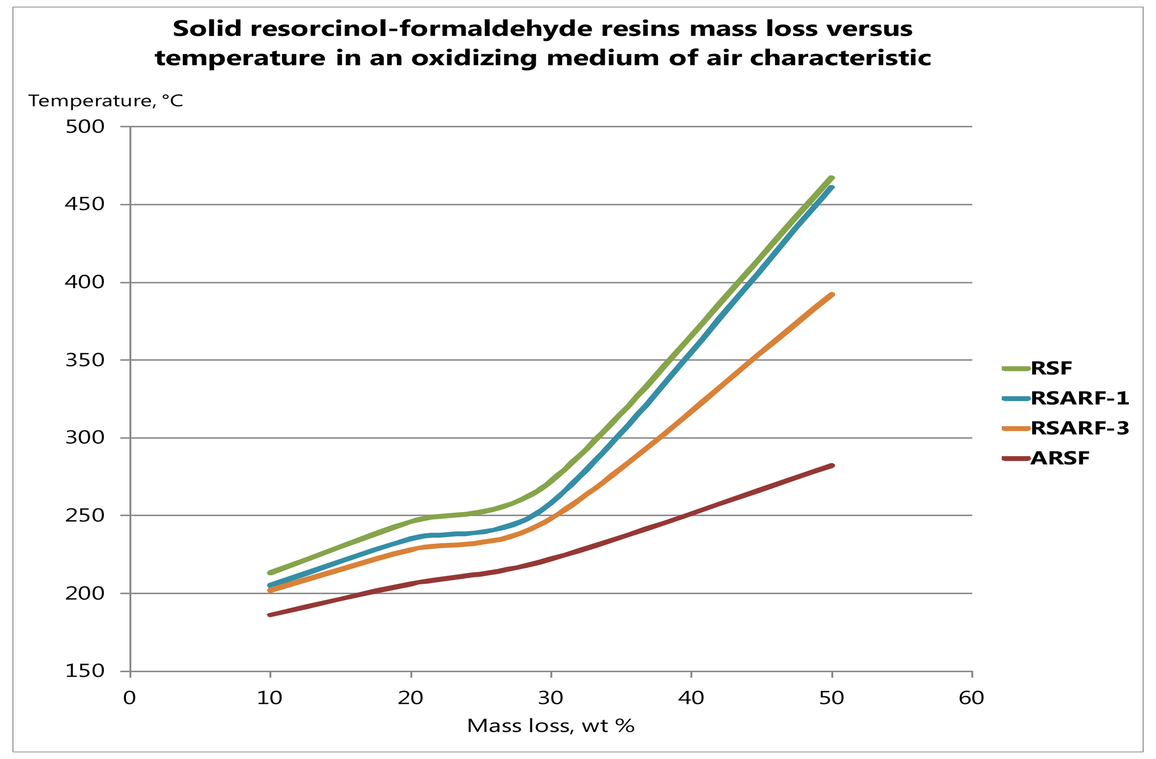
Physico-chemical characteristics of resorcinol-formaldehyde resins

Index	Method of analysis	Samples			
		RSF	RSARF-1	RSARF-3	ARSF
Volatiles content at 105 °C, wt %	ASTM E1868	0,6	0,4	0,6	0,9
Ash content, wt %	ASTM E1131	0,3	0,2	0,4	0,1
Coking value, wt%	TGA	24,0	23,9	19,4	13,8

When heating the resins in an inert atmosphere up to 830°C they are not exposed to complete decomposition. Their partial carbonization occurs, which is characterized by coking value. With increase of alkylresorcinols part in the formulation of the resin decrease of the resin's carbonization ability is observed.

The resins derived from oil shale phenolic fraction (ARSF) and modified by styrene have the highest content of volatile components. Replacing a small part of resorcinol with oil shale alkylresorcinols can lead to decrease of volatile components at 105 °C by 1.5-2 times. Ash content of the synthesized resins is in the range from 0.1 to 0.4 wt %.





Data of dynamic thermogravimetric analysis

Samples	Decomposition temperature depending on the loss of mass, °C							
	N_2				Air			
	τ_{10}	τ_{20}	τ_{30}	τ_{50}	τ_{10}	τ_{20}	τ_{30}	τ_{50}
RSF	201	236	255	291	213	246	272	467
RSARF-1	196	229	253	290	205	235	258	461
RSARF -2	201	227	247	291	202	228	248	392
ARSF	196	219	235	268	186	206	222	282

RSF and RSARF-1 resins are characterized by the highest thermal stability in long-term storage and have τ_{50} = 467 °C and τ_{50} = 461 °C, respectively. Increase of a part of oil shale alkylresorcinols fraction in the formulation of the resin leads to decrease of its thermal stability and the maximum rate of decomposition.

Replacement of resorcinol by a fraction of oil shale alkylresorcinols (10-100%) reduces the half-life period (τ_{50}), which characterizes the thermal stability of the product during long-term storage.

RSF, RSARF-1, RSARF-3 resins have similar behavior in an inert atmosphere. This can be explained by the formation of such polymeric structures for the above resins which are exposed to inessential impact of high temperatures in an inert atmosphere.

CONCLUSION

The obtained results show that ARSF resin is the least thermally stable and more prone to oxidative effect of atmospheric oxygen.

For the resin RSARF-3 decrease of thermal oxidative stability is observed.

Thermal properties of RSARF-1 resin remain unchanged compared to the RSF when adding 10% of oil shale alkylresorcinols into formulation instead of resorcinol.

Using TGA method it was established that the resin RSF, RSARF-1, RSARF-3 resins have similar behavior in an inert atmosphere.

Research of thermal characteristics of the synthesized solid resorcinol-alkylresorcinol-formaldehyde resins confirms the possibility of partial re-placement of resorcinol by oil shale alkyresorcinols with boiling point of 270 °C. These resins can be used in similar for RSF industries.