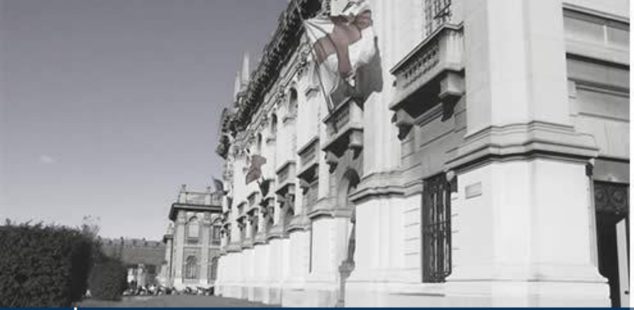

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POLITECNICO DI MILANO





High Efficiency ORC for High Temperature Molten Salt Boiler for Biomass Application

GECoS – Group of Energy COnversion Systems

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ENEA

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Summary

- Field of application
- Heat transfer fluid: molten salt
- Wood-fired boiler

- Working fluids
- Plant characterization
- Cycles simulations
- Results
- Conclusions & future works

Field of application

Climate and Energy package of the European Commission
(Dir. 2009/28/EU, Road Maps 2030 and 2050)
→ increase of energy production from renewables, heat in particular

goals for bioenergy:

- ✓ use of biomass in CHP plants, with good exploitation of heat (DH, …)
- ✓ distributed generation (need for technologies ≤ 1 MW_{el})
- ✓ increase of electric efficiency (lower than fossil fuels)
- ✓ reduction of emissions
- ✓ multiple renewable energy sources (i.e. biomass and solar)

ENEA, together with Research Institutes and Universities, is working on:

- local planning of biomass-to-energy pathways
- improvement of the overall efficiency of energy conversion

(funded by Italian Electrical System Research)

Field of application

Research activity on **the feasibility of innovative wood-fired CHP systems up to 1 MW_{el} (molten salts boiler + ORC)**

*Why **molten salts**?*

good thermal carriers and heat storage capacity

possibility to couple concentrated solar power systems (CSP) with biomass fired-boilers

→ need for stable and low freezing point mixtures (T 200÷500 °C)

*Why **ORC**?*

consolidated and reliable technology for wood-fired CHP plants in the power range of interest (up to 1 MW_{el})

→ need to improve η_{el} **(> 20%)** and to work at higher **T** (up to **450°C**)

Molten salts

Analysis of binary and ternary mixtures in **200÷500 °C**

- $NaNO_3/KNO_3$ (60:40 %w, “solar salt”)
- $Ca(NO_3)_2/NaNO_3/KNO_3$ (42,2:15,3:42,5 %w)
- $NaNO_3/KNO_3/NaNO_2$ (7:53:40 %w)
- $LiNO_3/NaNO_3/KNO_3$

✓ good thermal properties (as thermal carries and heat storage)

✓ low environmental impact

✓ low price (except Li)

Investigation of thermodynamic properties:

thermal stability, freeezing point (liquidus), heat capacity, viscosity, density, thermal conductivity

Molten salts

$NaNO_3$ [%w]	KNO_3 [%w]	$Ca(NO_3)_2$ [%w]	$LiNO_3$ [%w]	$NaNO_2$ [%w]	liquidus T [°C]	Max T [°C]	Cp [J/ (K g)]	µ [cP]	P [g/ml]	k [W/(K m)]
60	40				238	550÷600	1,6 [3]	≈4.5÷1,6 [3]	1,95÷1,7 [4]	≈0,5 [1]
7	53			40	141	450/538	≈1,55 [1]	10.5÷1,6 [1]	≈2 [1]	≈0,85 [2]
15	42	42			140	505	1,7÷1,6 [3]	200÷3,5 [3]	na	na
18	53		30		120	550÷600	≈1,55 [1][3]	30÷1,5 [1] [3] [a]	1,95÷1,7 [1]	na
18	40	21	22		<95	na	≈1,55 [1]	50÷4,5 [1] [a]	1,95÷1,7 [1]	≈0,45 [1]

Some data are extrapolated, they don't cover the whole T range

[a] extrapolated value

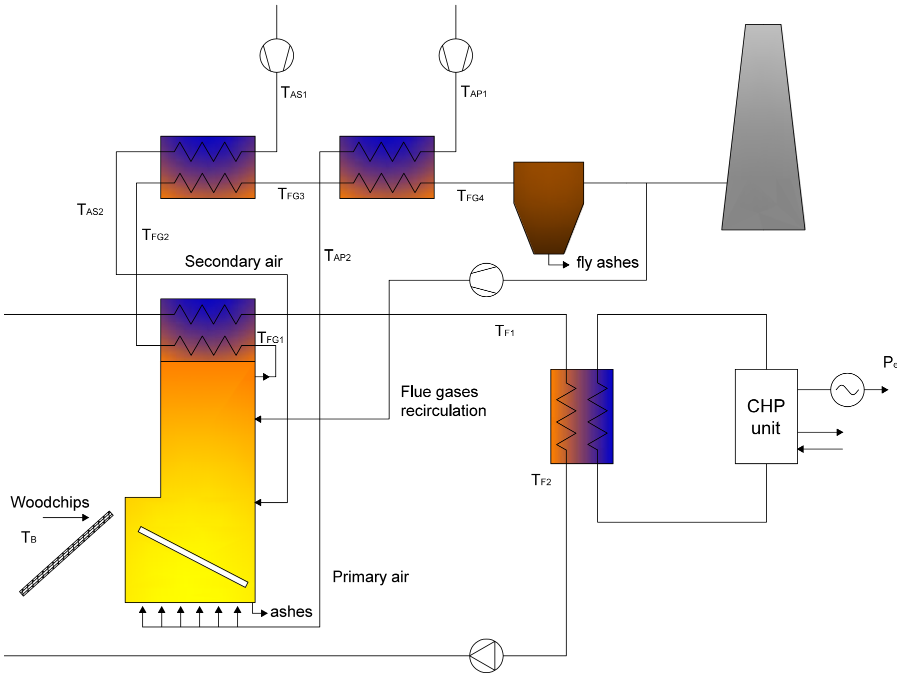
[1] Siegel N., Glatzmaier G. - Molten Salt Heat Transfer Fluids and Thermal Storage Technology - CIMTEC 2010, 5th Forum on New Materials – Montecatini Terme, Italy, 2010
[2] Coastal Chemical Co., L.L.C.. – HITEC® Heat Transfer Salt technical brochure
[3] ENEA experimental data
[4] Bradshaw R.W. - Effect of composition on the density of multi-component molten nitrate salts - SANDIA report SAND2009-8221, December 2009

Wood-fired boiler with molten salts

Analysis of components and operating conditions:

- **heat exchanger** (solar salts-flue gases)
- **heat recovery** (from flue gases and from high-T molten salts)
- **pre-heating** of primary and secondary air
- flue gas recirculation
- **grid**

parameter	unit	value
O_2 in the flue gas	% vol	7÷9
T flue gas (in HX)	°C	≈ 950
T molten salts (out CHP unit)	°C	< 250
T molten salts (in CHP unit)	°C	500

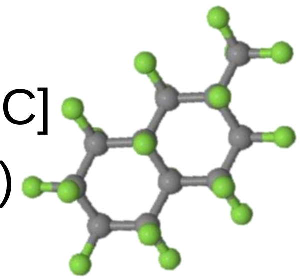


Procedure: Selection of working fluid

Main merit for the sought fluid is the thermal stability.

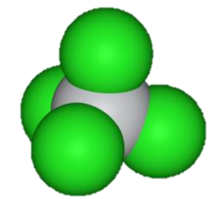
Organic compounds: Perfluorcarbons

- PP9: Perfluoro methyldecalin ($C_{11}F_{20}$) [Pc= 16.6 bar; Tc= 313.4°C]
  - high complexity molecule (limited cooling during expansion)
  - maximum tested temperature 420°C



Inorganic compounds:

- $TiCl_4$: Titanium tetrachloride [Pc=46.6 bar; Tc=364.8°C]
  - low complexity molecule
  - thermal stability proven over 1000°C

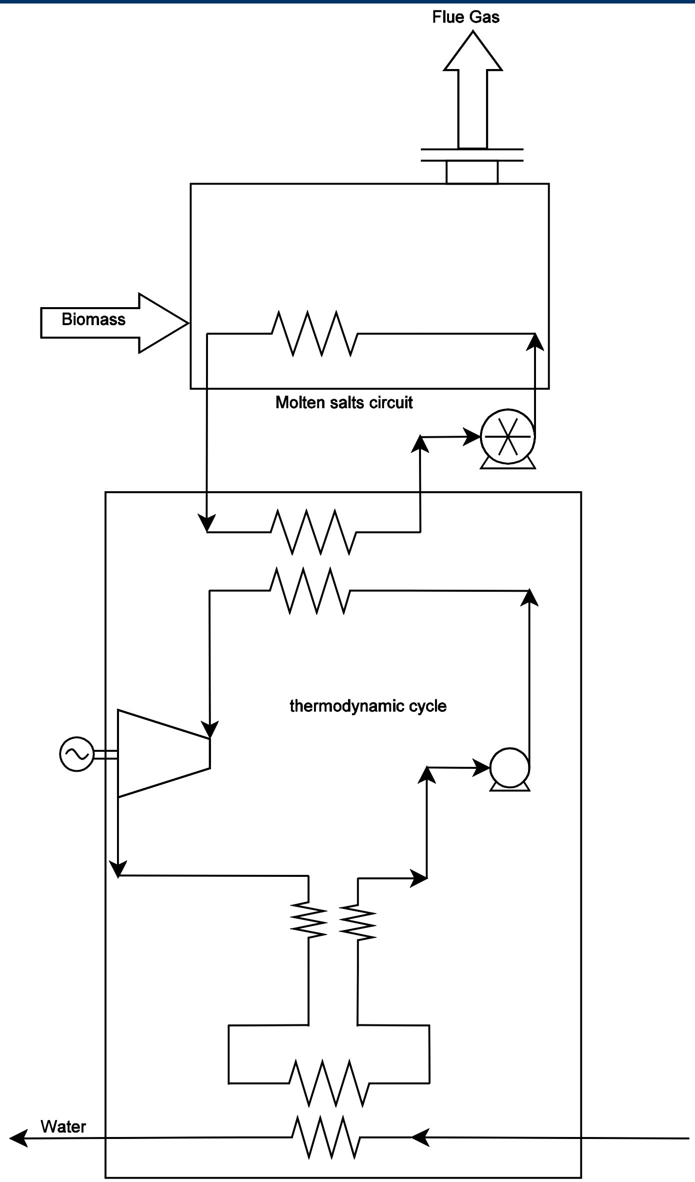


	PP9	$TiCl_4$
Thermodynamic Properties	+	++
Toxicity	++	-
Corrosiveness	++	-
Explosiveness	++	-
GWP	-	++
ODP	+(+)	++
Turbine Design	-	++
Heat exchanger Design	(+)	(+)
Price	--	+
Availability	-	+

Legend: ++ extremely positive, + positive, - negative, -- extremely negative

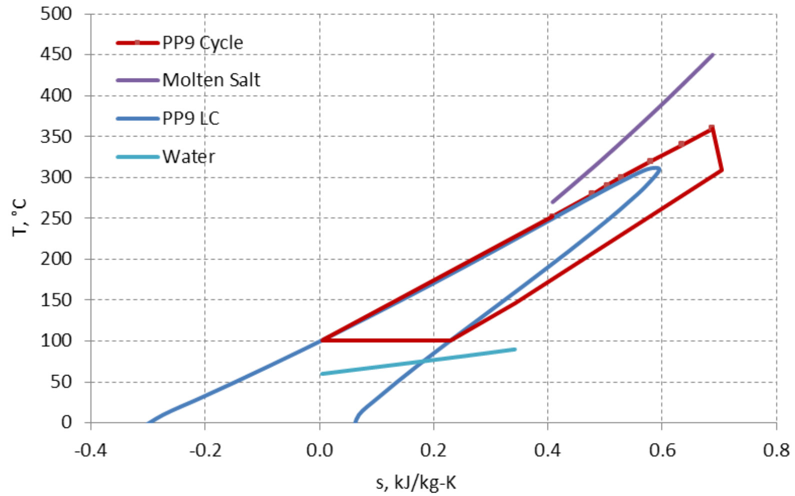
Cogenerative ORC

Parameter	Unit	Value
Salt temperature		
Inlet temperature	°C	450
Cogeneration water		
Inlet temperature	°C	60
Outlet temperature	°C	90
Minimum ΔT in heat exchangers		
Primary heat exchanger	°C	15
Condenser	°C	10
Regenerator	°C	20
Turbine		
Isoentropic efficiency	%	80
Electro-mechanical efficiency	%	95
Generator efficiency	%	97
Pumps		
Hydraulic efficiency	%	70
Electro-mechanical efficiency	%	95



PP9 simulated with Aspen Plus

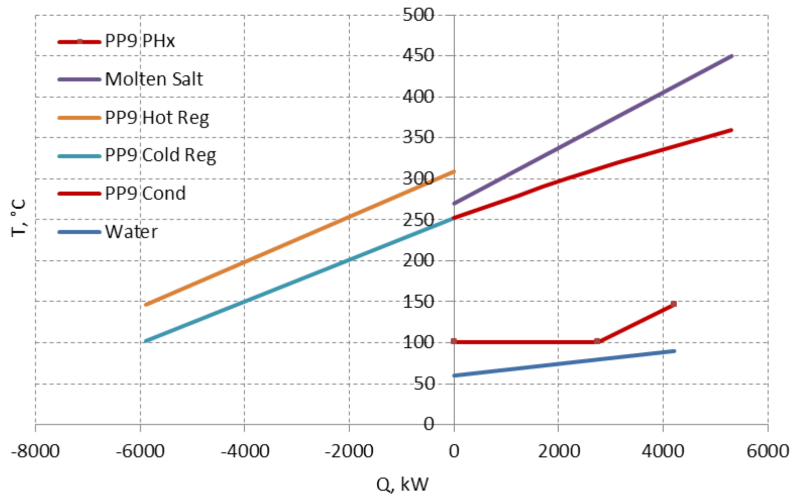
PP9 has been added in Aspen Plus components with UNIFAC Groups



Tmax salt: 450°C
Tmin salt : 270°C

Tmax PP9: 360°C
Pmax PP9: 25 bar

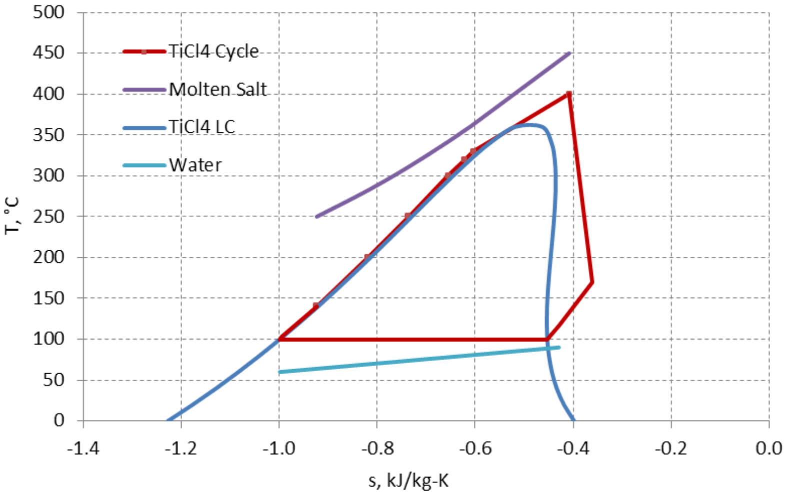
Thermodynamic properties has been calculated with Peng-Robinson EoS



PP9 large recuperator

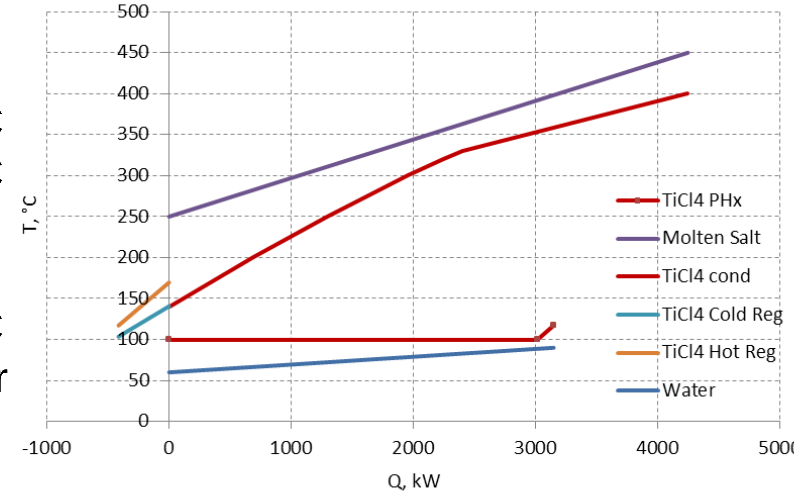
$TiCl_4$ simulated with Aspen Plus

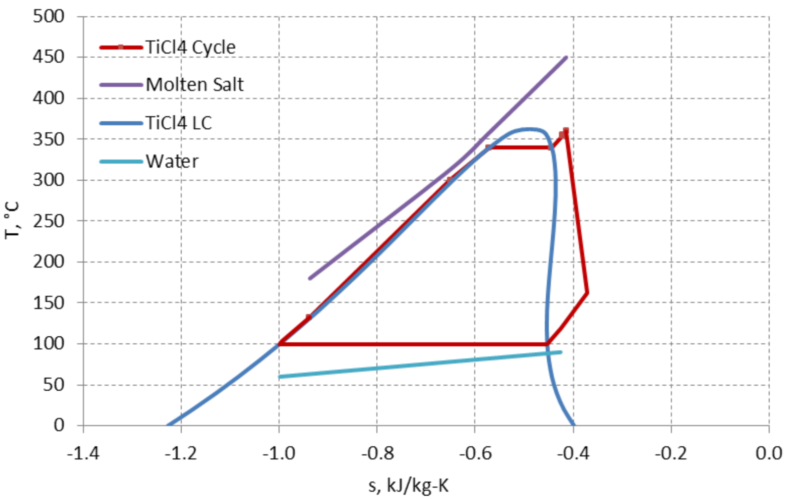
Thermodynamic properties has been calculated with Peng-Robinson EoS



Salt
Tmax: 450°C
Tmin: 250°C

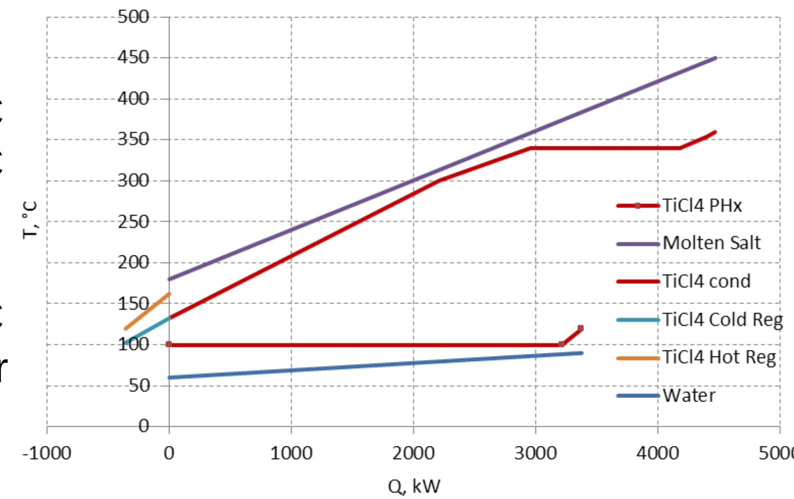
$TiCl_4$
Tmax: 400°C
Pmax: 50 bar





Salt
Tmax: 450°C
Tmin: 190°C

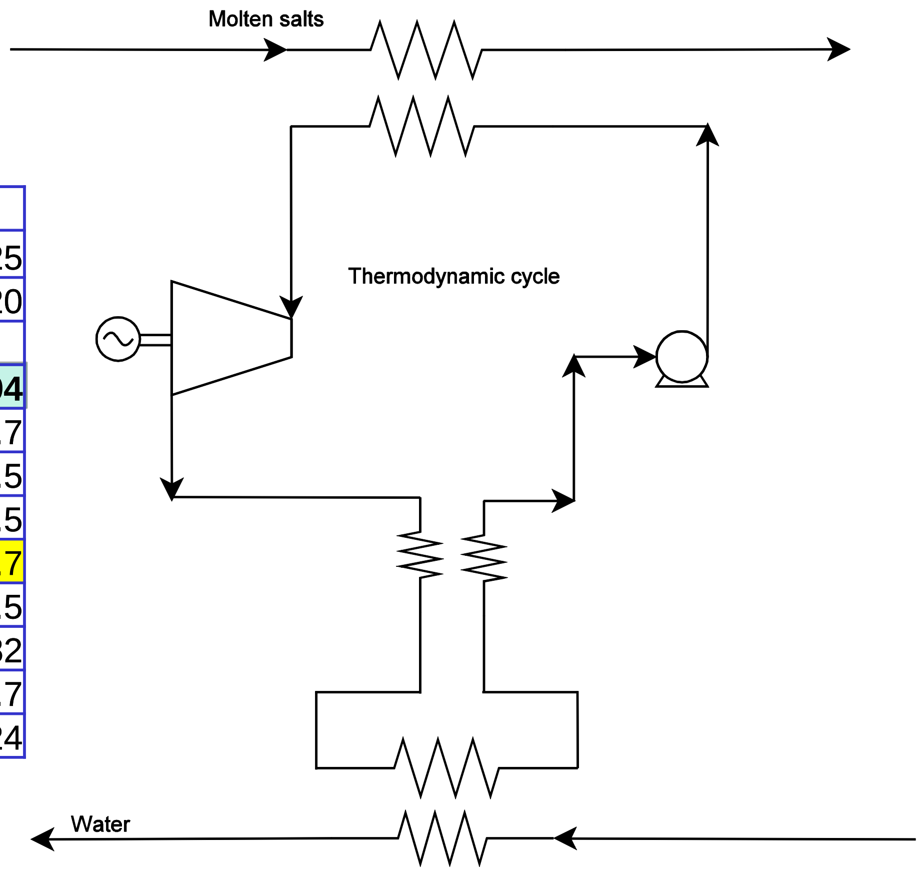
$TiCl_4$
Tmax: 360°C
Pmax: 35 bar



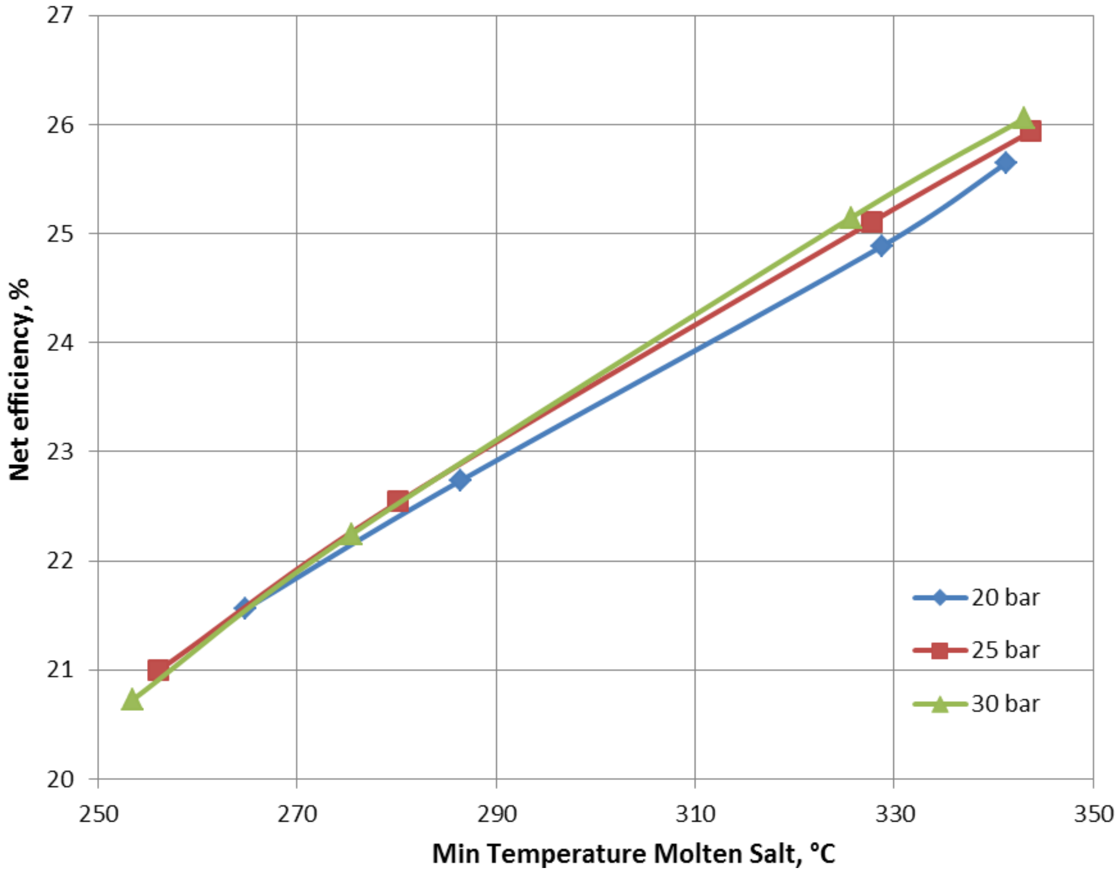
PP9 – Parametric studies

$$\eta_{\text{el\_Cycle,net}} = \frac{P_{el,turbine} - P_{el,pump}}{\dot{Q}_{in\ ciclo}}$$

Indipendent variables					
P Max	bar	25	25	25	25
T Max	°C	330	350	400	420
Results					
$\eta_{el\_cycle,net}$	**%**	**21.00**	**22.54**	**25.11**	**25.94**
Tout Rec	°C	241.1	265.2	312.7	328.7
DT hot	°C	155.5	182.8	238.8	259.5
DT cold	°C	140.9	165.0	212.5	228.5
T min salt	°C	256.1	280.2	327.7	343.7
UA Rec	kW/K	288.2	297.4	311.1	313.5
Power @ Recuperator	kW	6210	6743	7813	8182
(Vout/Vin)turb	-	470.6	333.8	225.0	209.7
Δh is, turb	kJ/kg	39.31	42.86	49.11	51.24



PP9 Results



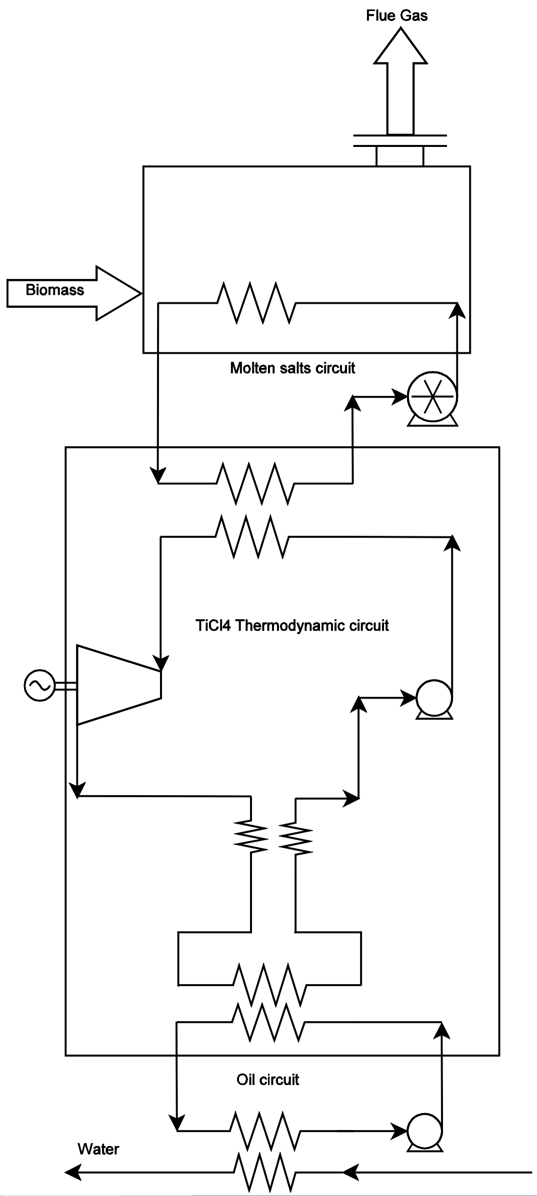
Efficiency higher than 20% for supercritical cycles and Tmin molten salts higher then about 240°C

Tmin salt limits recuperative heat

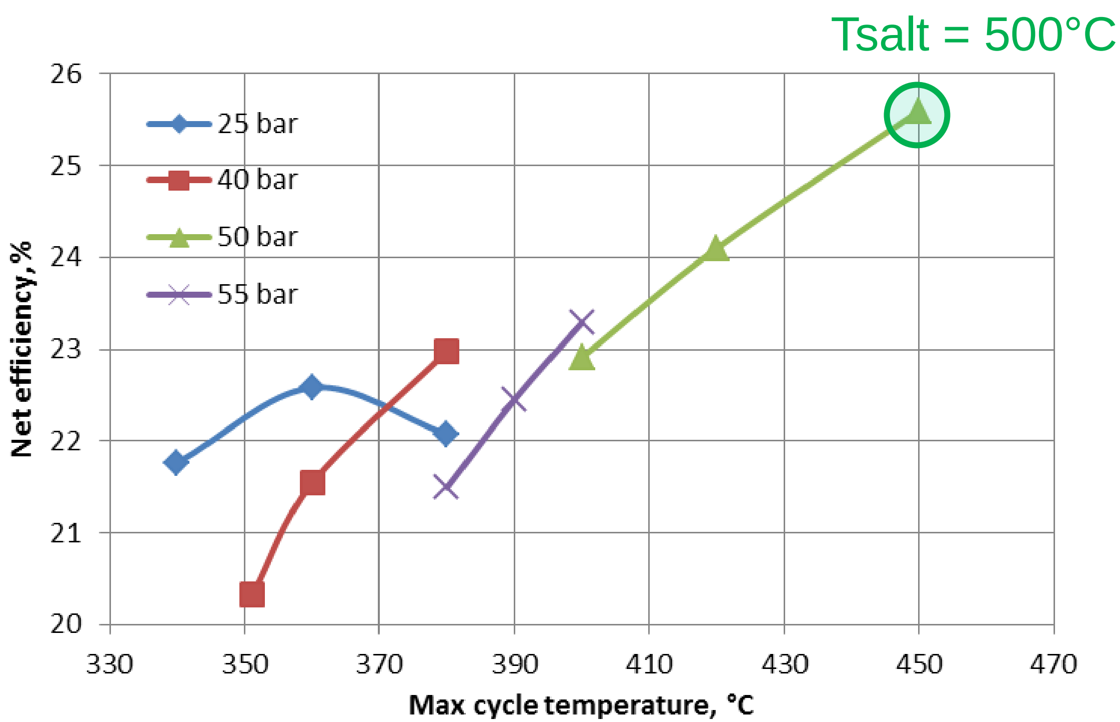
Scheme of plant $TiCl_4$

Indipendent variables				
P Max	bar	50	50	50
T Max	°C	400	420	450
Results				
$\eta_{el\_cycle,net}$	**%**	**22.91**	**24.1**	**25.6**
Tout Rec	°C	148.0	163.1	183.2
DT hot	°C	55.1	76.6	105.6
DT cold	°C	38.8	53.8	74.0
UA Rec	kW/K	20.4	24.0	27.0
Power @ Recuperator	kW	452.9	590.3	751.9
(Vout/Vin)turb	-	136.2	125.6	116.25
Δh is, turb	kJ/kg	95.0	101.3	109.4

Due to reactivity with water, a possible scheme of plant, adopots a oil circuit



$TiCl_4$ Results



Higher cycle temperatures require higher temperature of molten salts

Conclusions and future works

- Biomass fired molten salt boiler is considered.

- Molten salt is the source at variable temperature for ORC.
- Two fluids, new for ORC-purpose, are considered:
  - both cycles with PP9 and $TiCl_4$ can reach almost 26% of net efficiency
  - PP9, due to its high molecular complexity, does not couple as well as $TiCl_4$ to variable temperature source.

- PP9 requires high recuperative thermodynamic cycle.

- Due to the dangerous reaction of $TiCl_4$ with H_2O more precautions must be considered when it is employed.

Next steps will focus on:
- the dimensioning of components
- design of the wood-fired molten salts boiler
- performance evaluation for a whole plant
- full-electric applications
- economic assessment
- pilot plant testing

THANK YOU