USING FACTSAGE TO STUDY THE BEHAVIOR OF INORGANIC MATTER IN THERMAL CONVERSION OF BIOMASS

GTT-Technologies'18th Annual Users' Meeting June 29- July 1, 2016| F. Defoort

OUTLINE

1. **Introduction**
2. **Thermodynamic tools**
3. **Thermodynamic simulation**
   1. Volatilisation
   2. Ash behaviour
4. **Simplified tool to characterize biomass**
5. **Conclusions**

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INORGANIC MATTER OF BIOMASS

- **Many elements**
  - Al, As, B, Ba, Ca, Cl, Cd, Cr, Cu, Fe, Hg, K, Mg, Mn, N, Na, P, S, Ti, V, Zn, Zr

- **Main elements**
  - Biomass
    - Wood and woody biomass Ca, Si, **K**
    - Agricultural residues Si, **K**, Ca
  - Waste wood
    - Coated particulate panel Si, **Ti**, Ca
    - Painted wood **Ba**, Ti, Ca +**Zn**
    - Impregnated wood **Cu, Cr**, Ca (As)
  - Solid Recovery Residues Ca, Si, S, Al, Fe, **Na**

- **Minor elements** As, Cd, Hg, Pb…

PROBLEMATICS OF INORGANIC MATTER

- **Deposition on heat transfer surfaces**
  - Fouling
  - Corrosion of metallic part
- **Emissions of trace species and particles (aerosol)**
  - Harmful to health
  - Detrimental for catalyst

} Volatilisation

- **Slag formation in furnaces**
  - Desirable for entrained flow reactor
  - Undesirable for grate furnace and fluidized bed reactor
- **Bed agglomeration in fluidized beds**
  - Defluidization

} Liquid

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THERMODYNAMIC TOOLS

- **Shared by several laboratories at CEA Grenoble**
  - microelectronics, batteries, material sciences, solar, **biomass**…
- **Software based on minimization of the gibbs free energy**
  - Factsage 7.0
- **Databases**
  - FACT databases
    - pure substances (FT53 FactPS)
    - solutions FToxid, FTsalt, FTmisc, FThall, FThelg, FTpulp, FTfrtz and FTOxCN, FSstel, SGnobl)
  - GTT/FZJ databases (Tatjana Jantzen and Elena Yazhenskikh)
    - GTOX.4 (Al-Ca-Fe-Mg-K-Na-Si)
      - solid K-Ca and K-Mg silicates
    - GTOX.5 (+ Cr-Mn-P-S-Zn)

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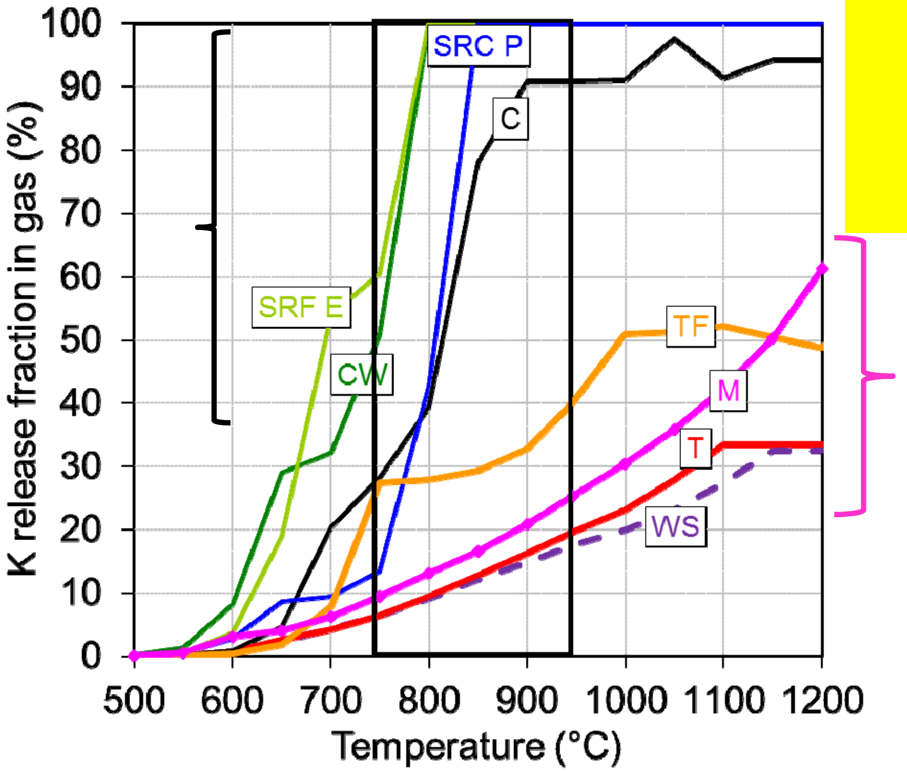
BIOMASS VOLATILISATION

- **Substances database → thermodynamic calculation of gas release**

Wei , Sonwane , Kuramochi , Mojtahedi , Thy , Turn , Froment , Stemmler, Jensen

High K release



Low K release

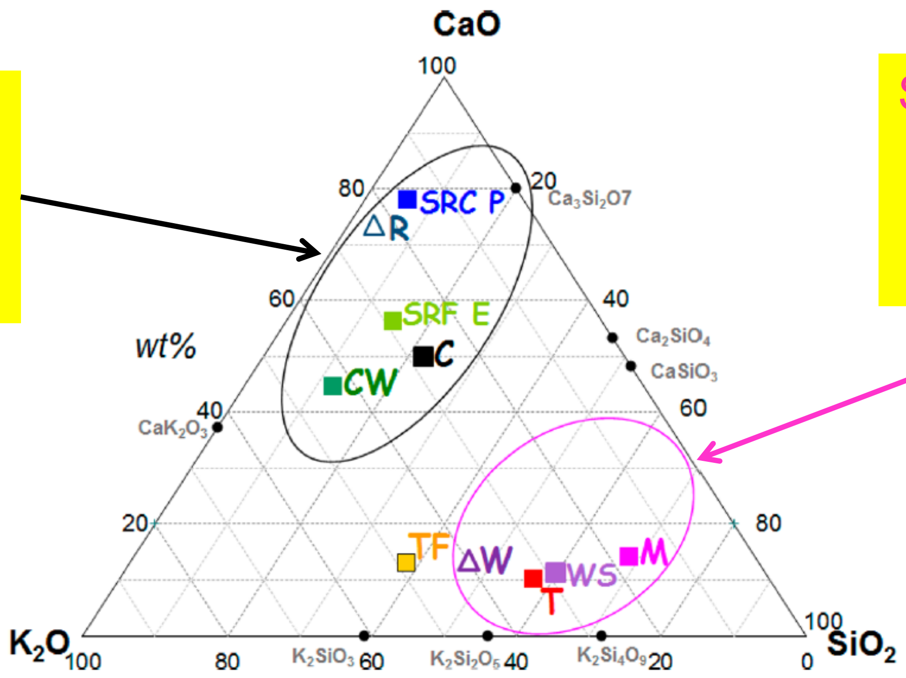
- Coniferous Wood (CW)
- Short Rotation Forestry of Eucalyptus (SRF E)
- Short Rotation Coppice of Poplar (SRC P)
- Wheat Straw (WS)
- mix of various by-products called Calys (C)
- annual crop Triticale (T)
- forage grass: Tall Fescue (TF)
- perennial crop: Miscanthus (M)

Published in Energy and Fuels 2015, 29, 7242-7253

BIOMASS VOLATILISATION

- **Composition of biomass**

Silica poor
High K release



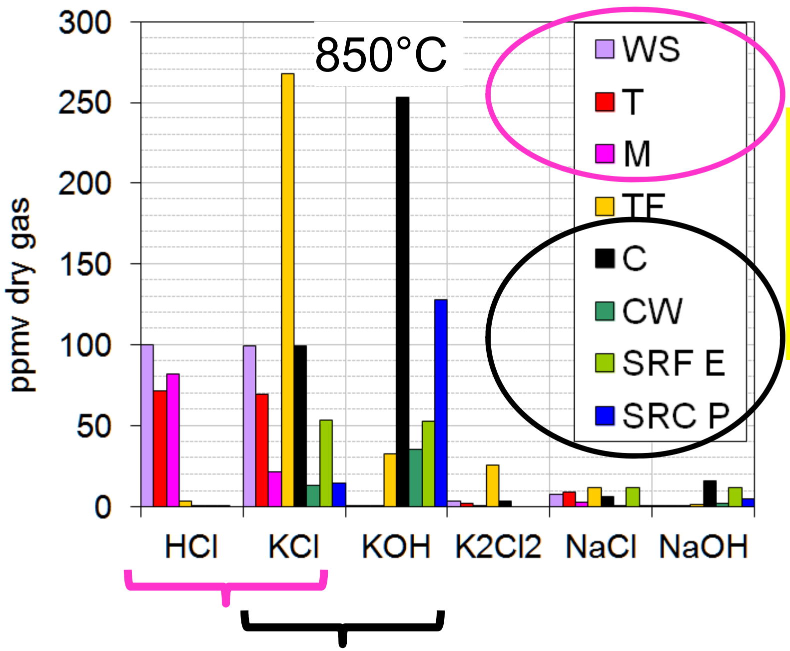
Silica rich
Low K release

- **Speciation of the gas phase?**
- **Comparison with experiments?**

BIOMASS VOLATILISATION

- Gas phase speciation calculated with substances database

Silica poor
High K release
KCl + KOH
K_2CO_3 deposit



Silica rich
Low K release
KCl + HCl
KCl deposit

BIOMASS VOLATILISATION

- **Gas phase speciation calculated with substances database**

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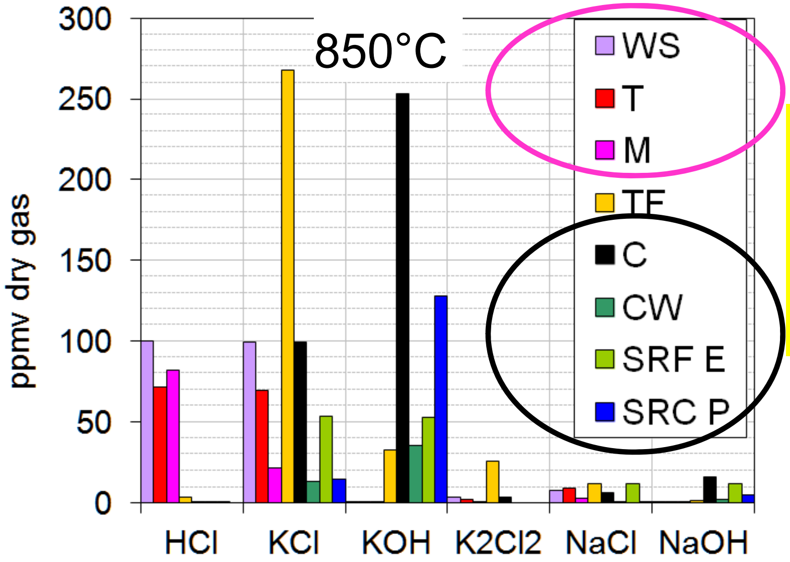

Silica rich
Low K release
KCl + HCl
KCl deposit

- **Experimental evidence of gas phase speciation**
  - Direct evidence
    - difficult to measure (MBMS)
  - Indirect evidence
    - deposit in Fluidized bed candle

Silica poor
KCl deposit

Silica rich
KCl deposit

Disagreement for silica poor

BIOMASS VOLATILISATION

- **Gas phase speciation calculated with different hypothesis**
  - Bed material effect, reducing environment, try several solution database (Ftoxid, GTOX)
  - Strongest effect→ use a solution database (liquid phase)

Silica poor biomass (Calys)

ppmv dry gas	Fact53 Pure substance	FTOX Slag A	GTOX.4 LIOX
HCl	0.1	0.4	0,9
KCl	99.5	95	81
KOH	253	93	40
% K in gas	78%	44%	29%

KOH(g) decreased

Indirect evidence: K_2CO_3 deposit calculated; KCl deposit calculated

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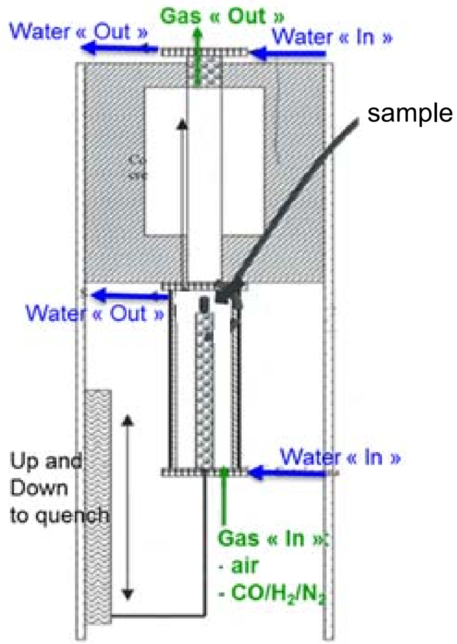
ASH BEHAVIOUR

- **Goal**

  Characterization of ash at the process temperature in oxidizing (combustion) or reducing (gasification) atmosphere
  - Check liquid occurrence

- **Methodology**
  - Experiments
    - biomass ashed
    - pressed in pellet (0,5 to 1g)
    - **annealed** 4 to 6 h in air or H_2/CO_2 at T
    - « **quench** »
    - SEM-EDX and XRD
  - Thermodynamic simulation
    - Database: GTOX.4, FTsalt, FactPS
    - Input data
      - mass and composition of pressed pellet
      - gas volume injected during annealing duration



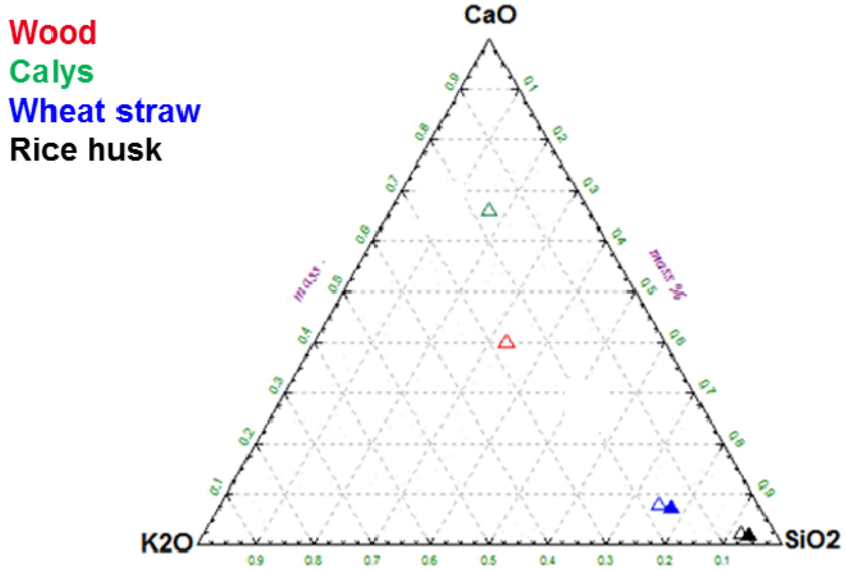
→ T<1300°C
→ N_2, air, $H_2/CO/CO_2$
→ 50 200 Nl/h
→ Quench : 2 to 20 °C/s

ASH BEHAVIOUR

- **Example four biomass ashes**
  - Boigelot & Al (22nd EUBC&E 2014 Hamburg 2BV.2.40, WasteEng 2014 Poster n°386)

Biomass dry ash content 815°C (wt%)	
Wood	0,2%
Calys	4,4%
Wheat straw	8,3%
Rice husk	14%

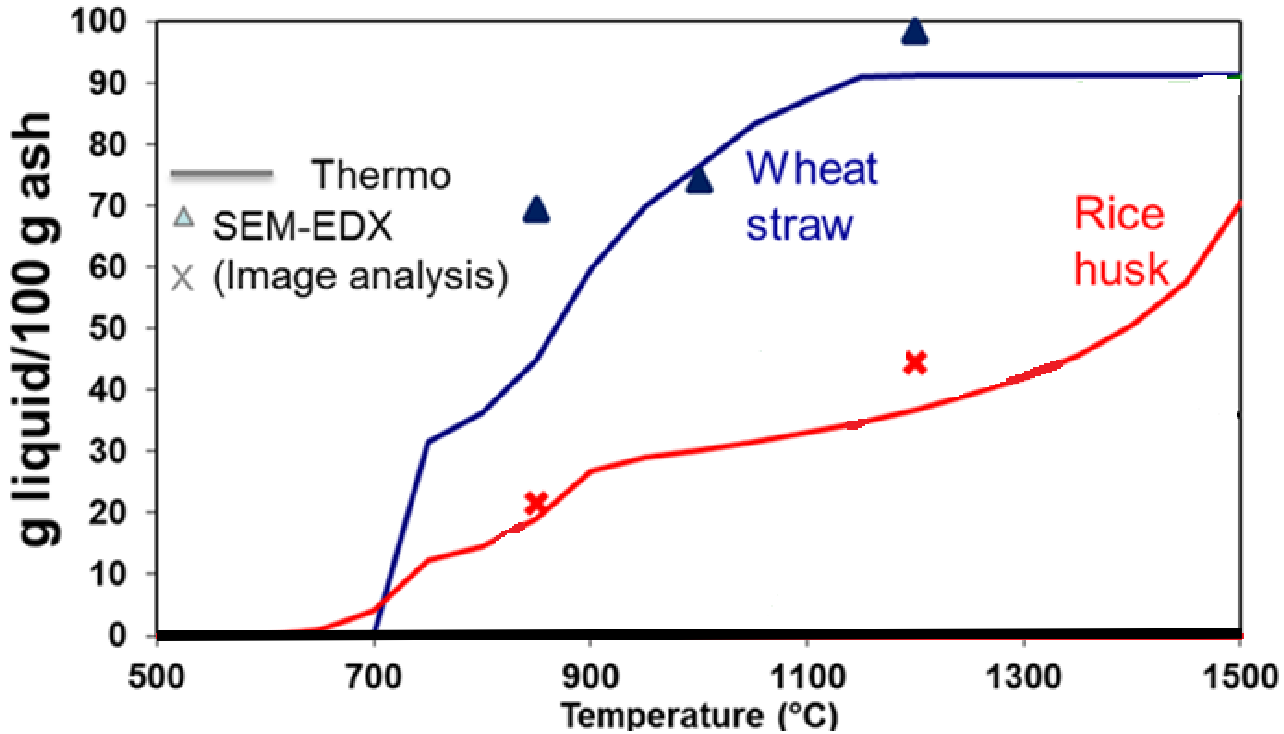
Ash content (wt%)	SiO_2	CaO	K_2O	Fe_2O_3	MgO	P_2O_5	Al_2O_3	Na_2O	TiO_2	MnO_2	ClO	SO_3	C
Wood	19,4	23,2	15,5	5,9	6,1	3,7	5,2	0,8	0,4	2,0	0,1	0,9	7,0
Calys	10,8	44,4	11,6	2,0	2,9	9,5	0,6	0,2	0,1	0,1	0,6	1,4	6,7
Weat Straw	65,4	7,0	14,5	1,4	1,6	3,7	0,6	0,4	0,1	0,1	0,9	1,1	3,0
Rice Husk	79,5	2,2	5,2	0,6	0,8	1,3	0,2	0,2	0,1	0,2	0,3	0,2	5,3



Boigelot & Al WasteEng Rio de Janeiro 2014 Poster n°386

ASH BEHAVIOUR

- **Liquid amount**
  - Good agreement with calculations for Wheat Straw and Rice husk
  - Not possible to quantify by SEM-EDS or XRD for Wood and Calys



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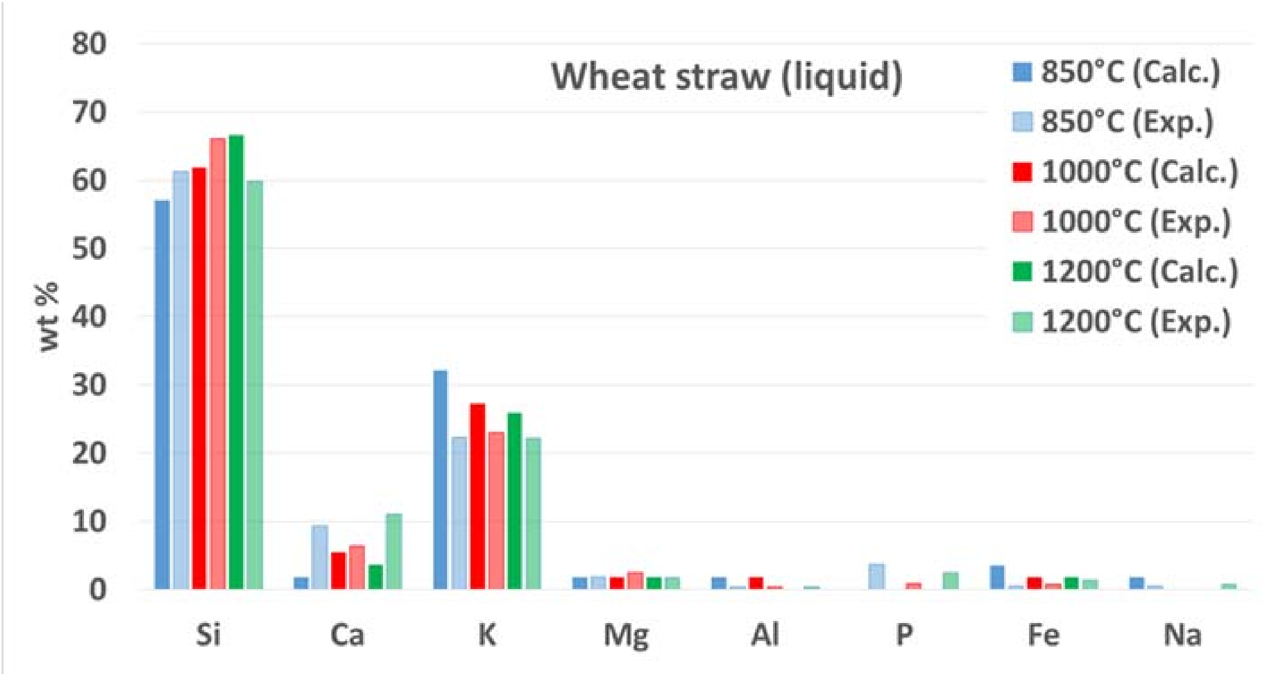
ASH BEHAVIOUR

- **Solid phase (XRD)**
  - Phosphates $Ca_xK_yPO_4$ $KCaFeP_xO_y$ (XRD) not existing in GTOX.4
  - K-silicates ($K_2Ca_2Si_9O_{21}$, $KFeSi_3O_8$) calculated not existing in XRD databases
- **Liquid composition**
  - For Wheat Straw and Rice husk calculation depleted in Si and Ca and enriched in K due to missing K_xCaP compounds/solutions in GTOX.4



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SIMPLIFIED TOOL TO CHARACTERIZE BIOMASS

- Thermodynamic equilibrium calculations with « equilib » module not very easy to carry out
- Simple tools are existing based on indices but are empirical
- Need a simple tool as scientific as possible

SIMPLIFIED TOOL TO CHARACTERIZE BIOMASS

- **We propose a tool based on**
  - Simplified ternary and quaternary phase diagram (isothermal section)
    - Ash composition
    - Process requirements

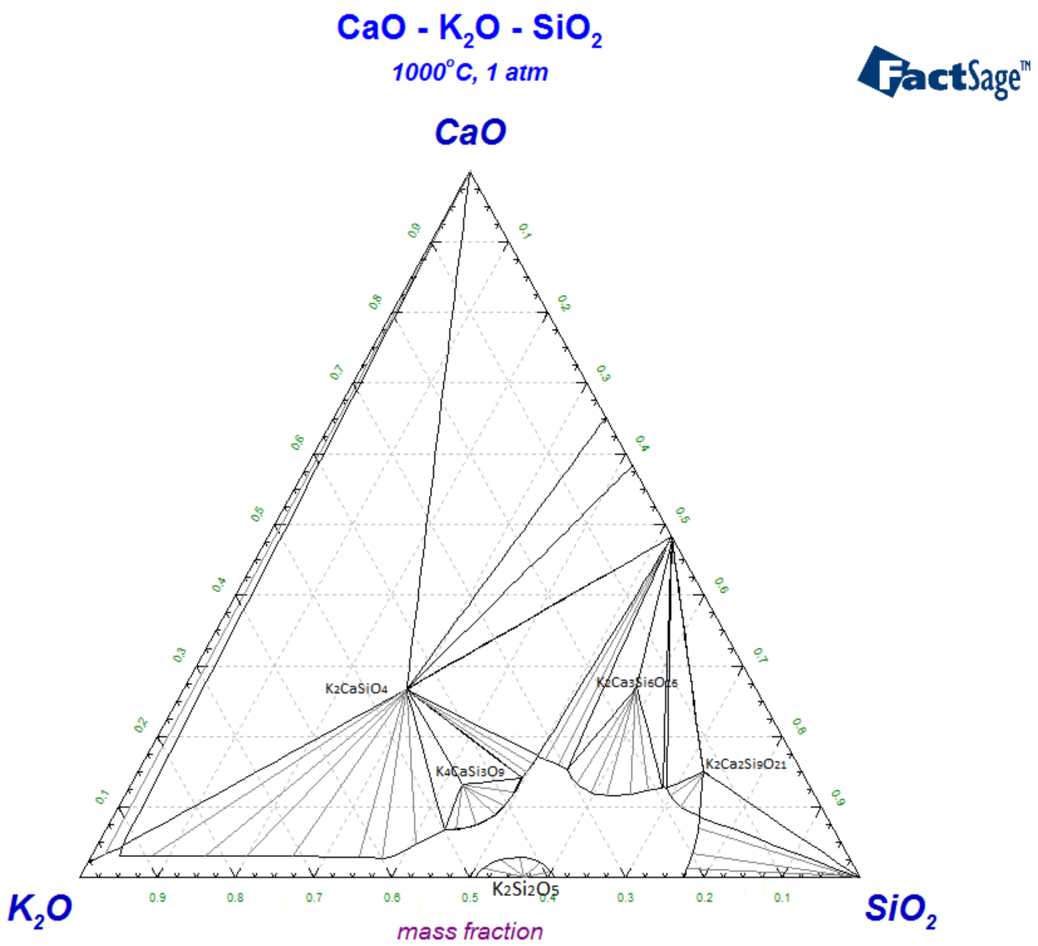
Fluidized Bed Reactor, Grate Boiler	Entrained Flow Reactor
100% solid (liquid undesirable) 850-1000°C	100% liquid 1200-1400°C

- **Computation with**
    - « Phase diagram » module of Factsage 7.0
    - GTT/FZJ database **GTOX.5**
    - 4 temperatures (850, 1000, 1200, 1400°C)
    - Main oxides: $CaO\text{-}K_2O\text{-}SiO_2\text{-}MgO\text{-}P_2O_5\text{-}Al_2O_3\text{-}Na_2O$

- **To be published in proceeding**
  - L. De Fusco, F. Defoort in Venice 2016 6th international symposium on energy from biomass and waste 14-17/11/2016

SIMPLIFIED TOOL TO CHARACTERIZE BIOMASS

- **Key ternary phase diagram**



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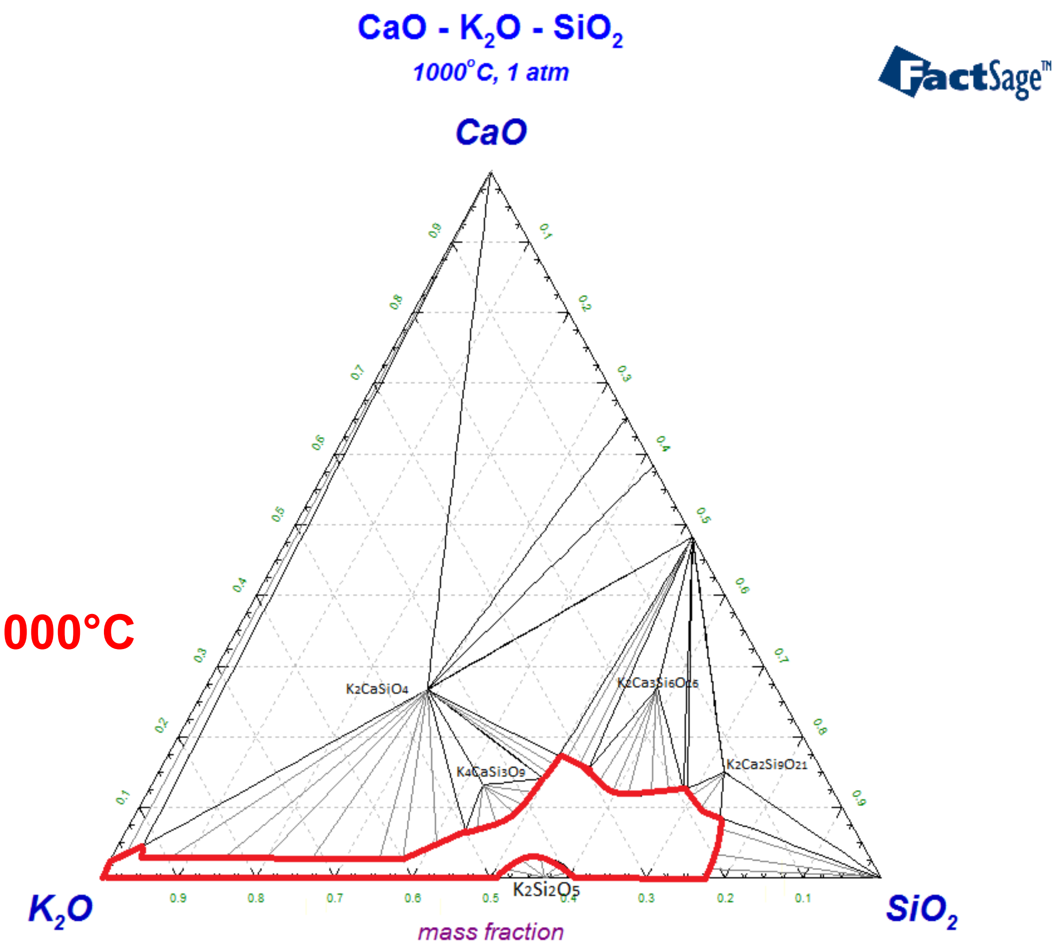

Liquidus line at 1000°C

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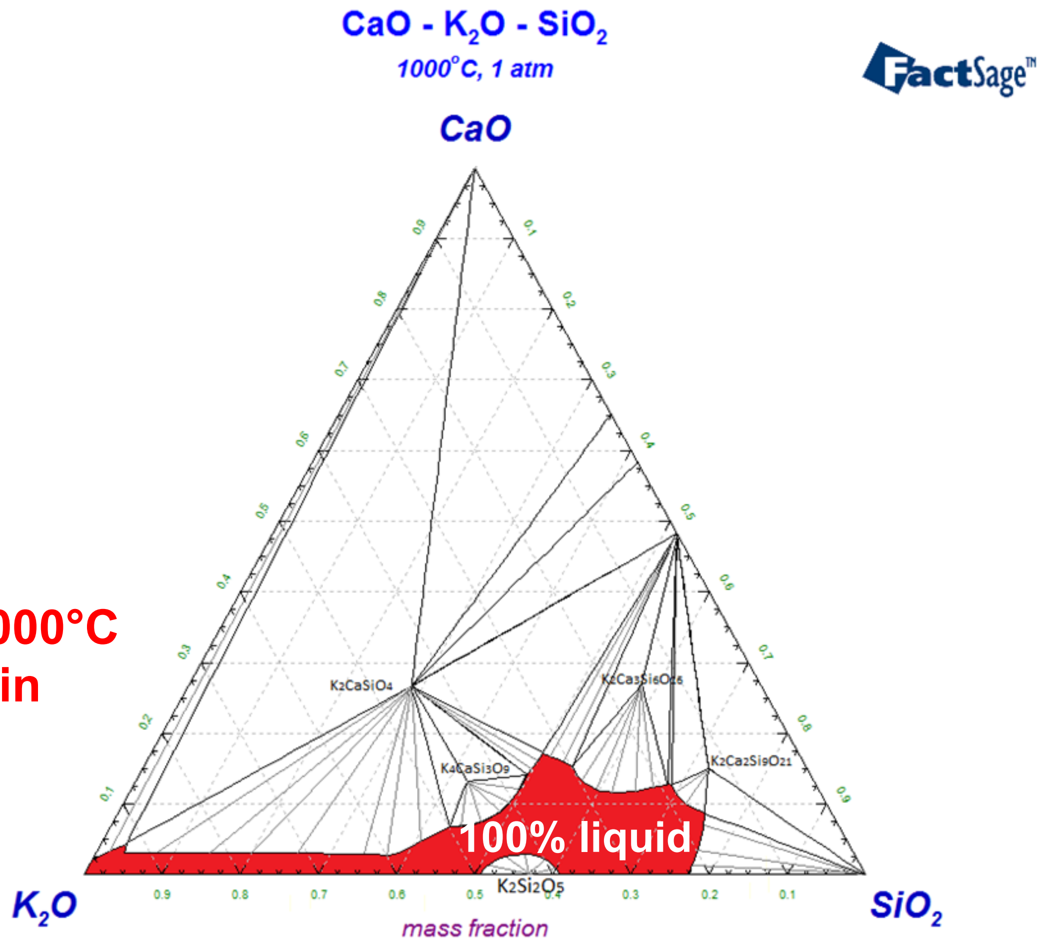
SIMPLIFIED TOOL TO CHARACTERIZE BIOMASS

- Key ternary phase diagram

Liquidus line at 1000°C
100% liquid domain



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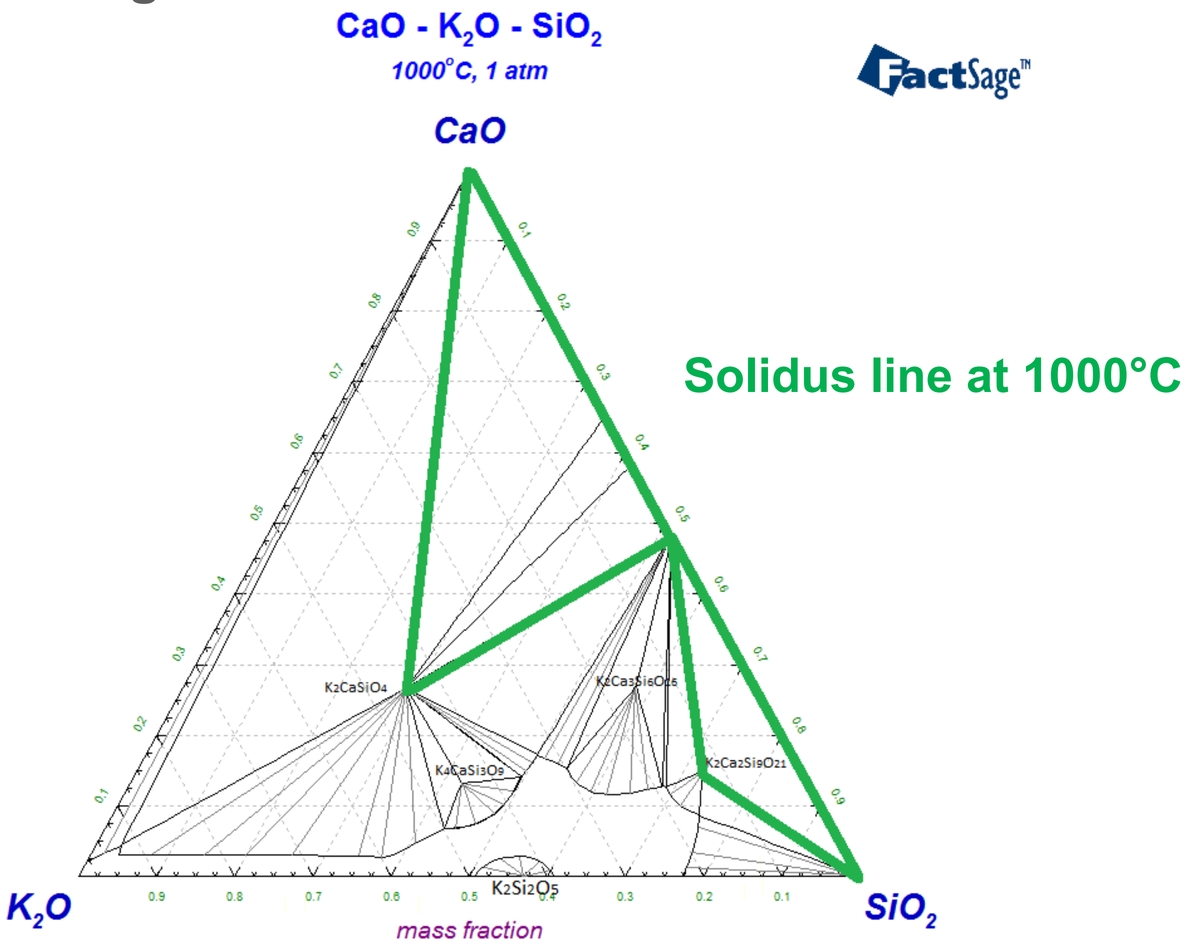

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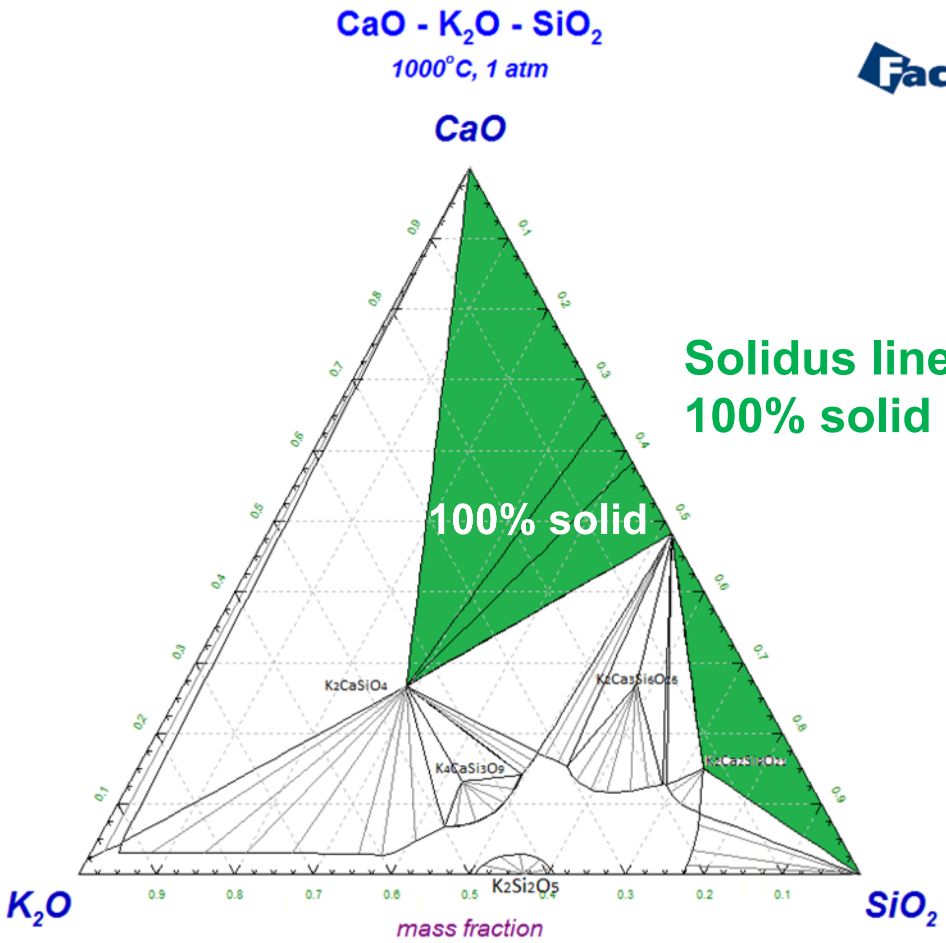

Solidus line at 1000°C
100% solid domain

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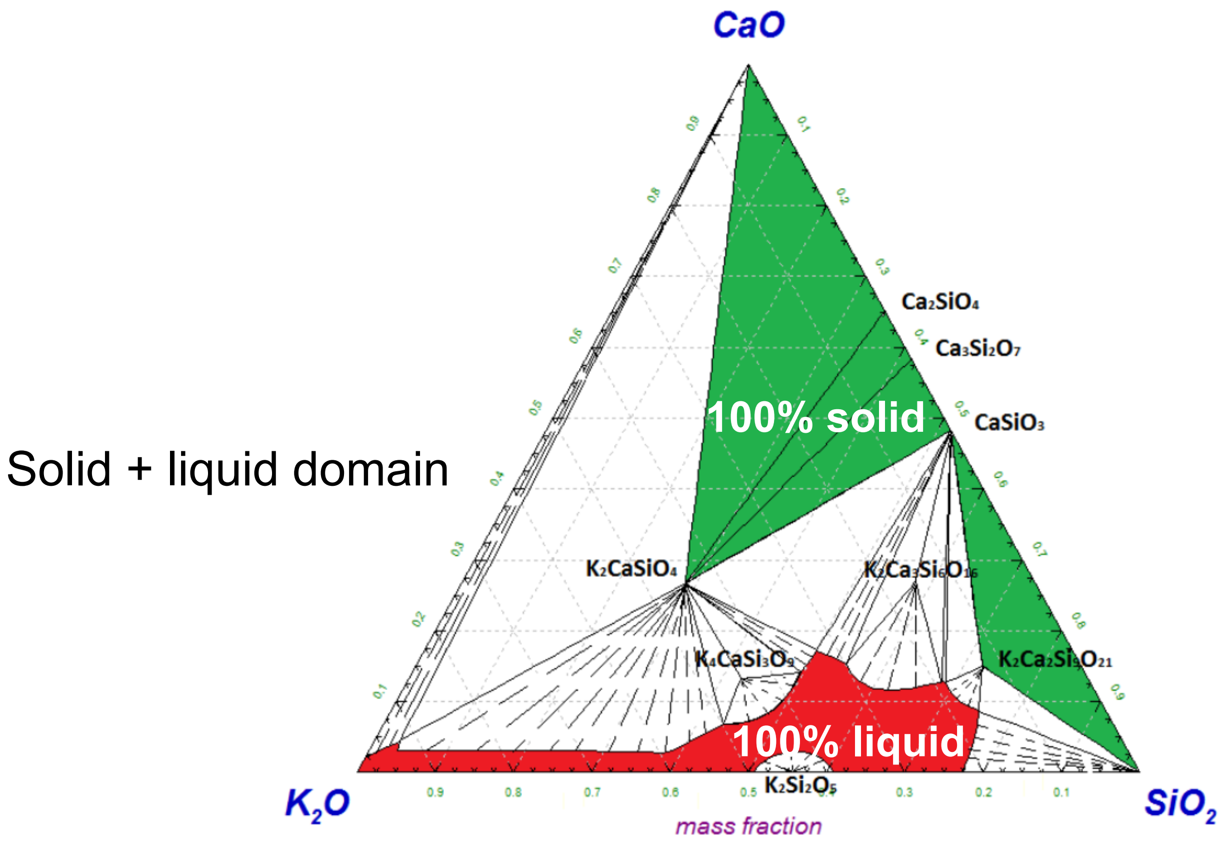

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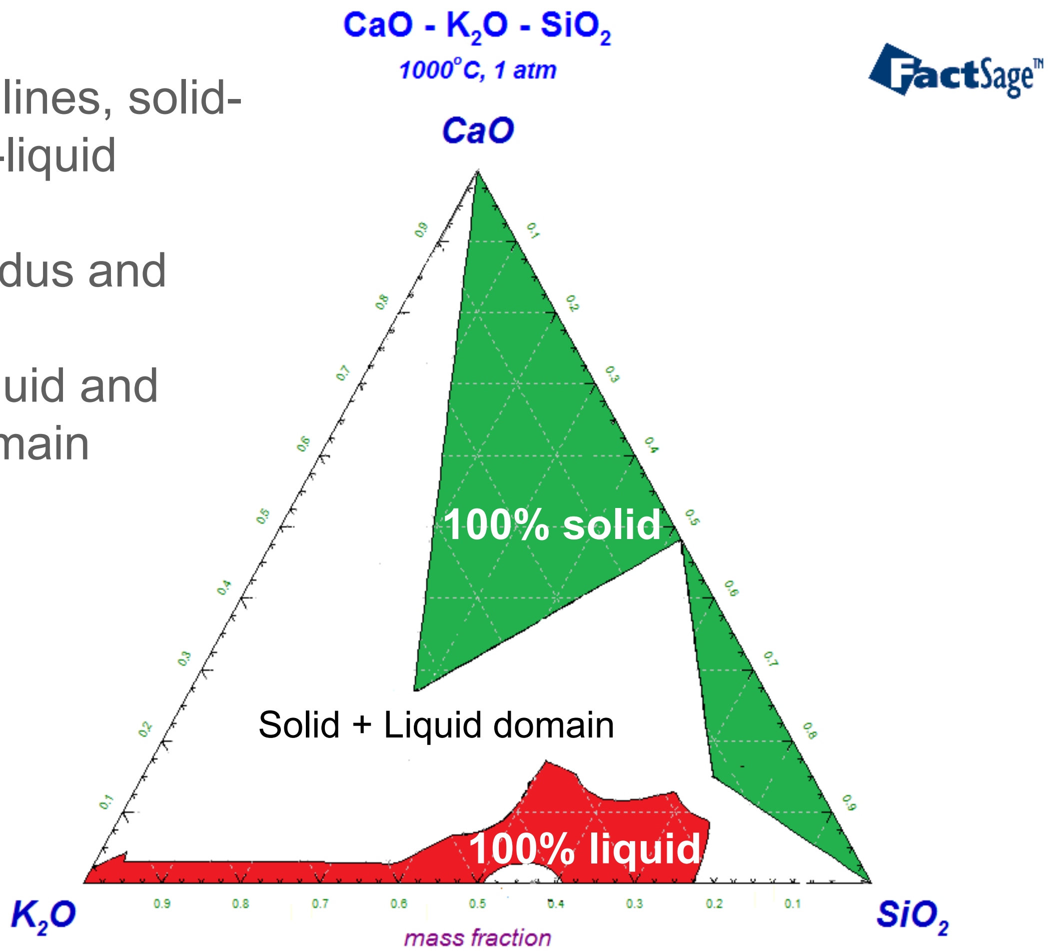
SIMPLIFIED TOOL TO CHARACTERIZE BIOMASS

- **Simplification of the phase diagram**
  - Remove all tie lines, solid-solid and solid-liquid equilibria lines
  - Keep only liquidus and solidus lines
  - Show 100% liquid and 100% solid domain



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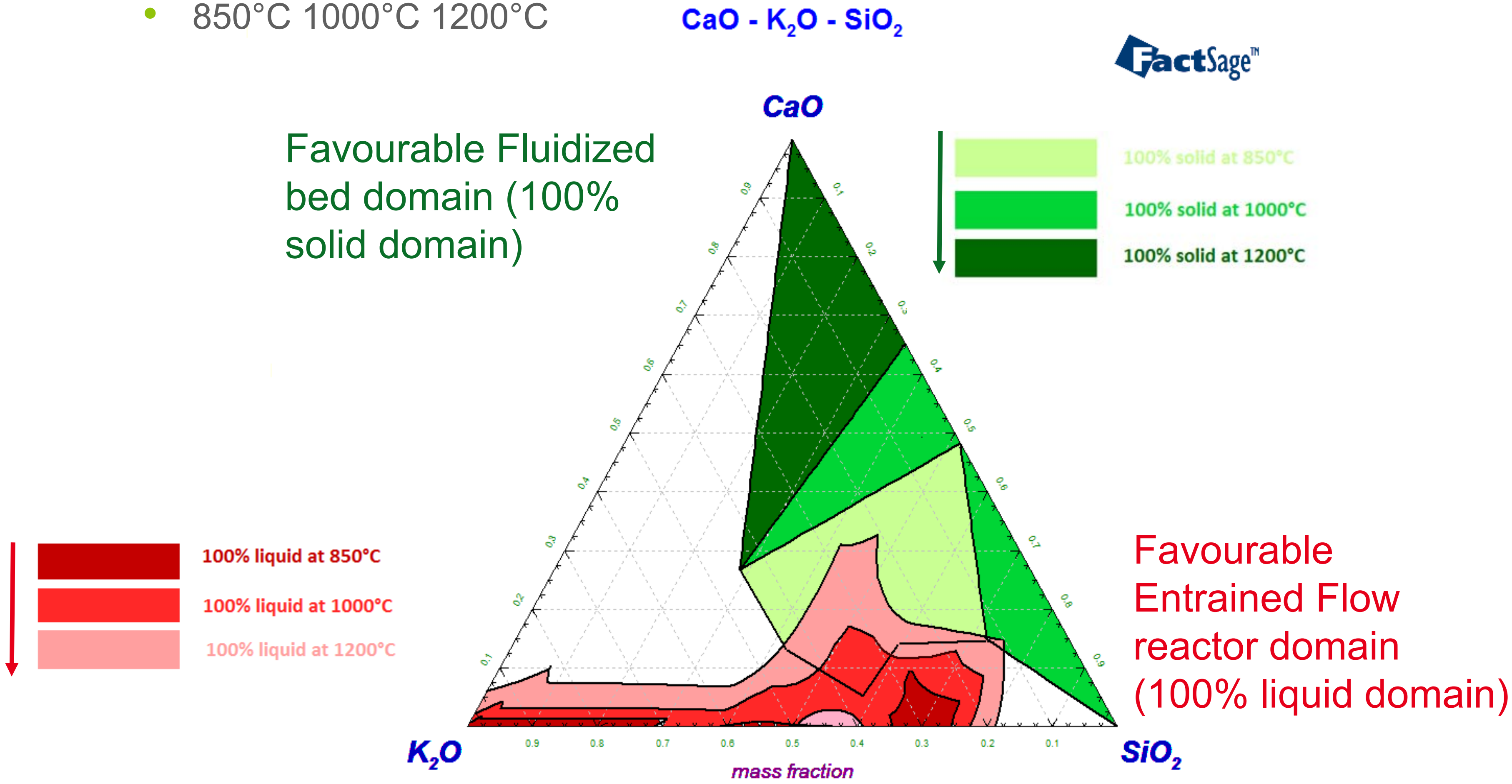
SIMPLIFIED TOOL TO CHARACTERIZE BIOMASS

- **Temperature effect represented in one diagram**
  - 850°C 1000°C 1200°C



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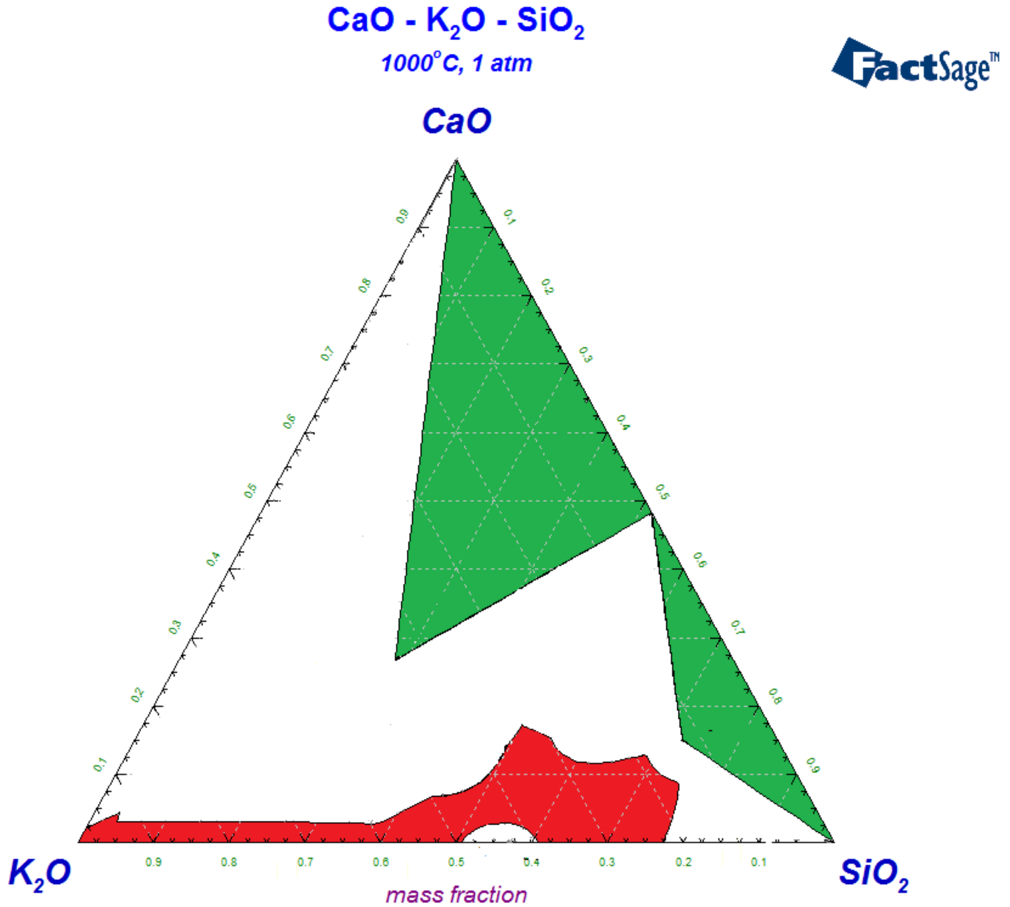
SIMPLIFIED TOOL TO CHARACTERIZE BIOMASS

- **Same representation calculated for 15 ternary phase diagrams**

Nr. #	Oxides			+10%	Temperature [°C]
1	CaO	**K_2O**	SiO_2	-	850; 1000; 1200; 1400
2	CaO	**K_2O**	P_2O_5	-	850; 1000; 1200
3	SiO_2	**K_2O**	Al_2O_3	-	850; 1000; 1200
4	MgO	**K_2O**	P_2O_5	-	850; 1000; 1200
5	MgO	**K_2O**	SiO_2	-	850; 1000; 1200
6	CaO	**P_2O_5**	SiO_2	-	850; 1000; 1200
7	CaO	**P_2O_5**	FeO	-	850; 1000; 1200
8	SiO_2	**P_2O_5**	Al_2O_3	-	850; 1000; 1200
9	MgO	**P_2O_5**	FeO	-	850; 1000; 1200
10	MgO	**P_2O_5**	SiO_2	-	850; 1000; 1200
11	CaO	**Na_2O**	SiO_2	-	850; 1000; 1200
12	CaO	**Na_2O**	P_2O_5	-	850; 1000; 1200
13	SiO_2	**Na_2O**	Al_2O_3	-	850; 1000; 1200
14	MgO	**Na_2O**	P_2O_5	-	850; 1000; 1200
15	MgO	**Na_2O**	SiO_2	-	850; 1000; 1200

SIMPLIFIED TOOL TO CHARACTERIZE BIOMASS

- **Quaternary diagram**



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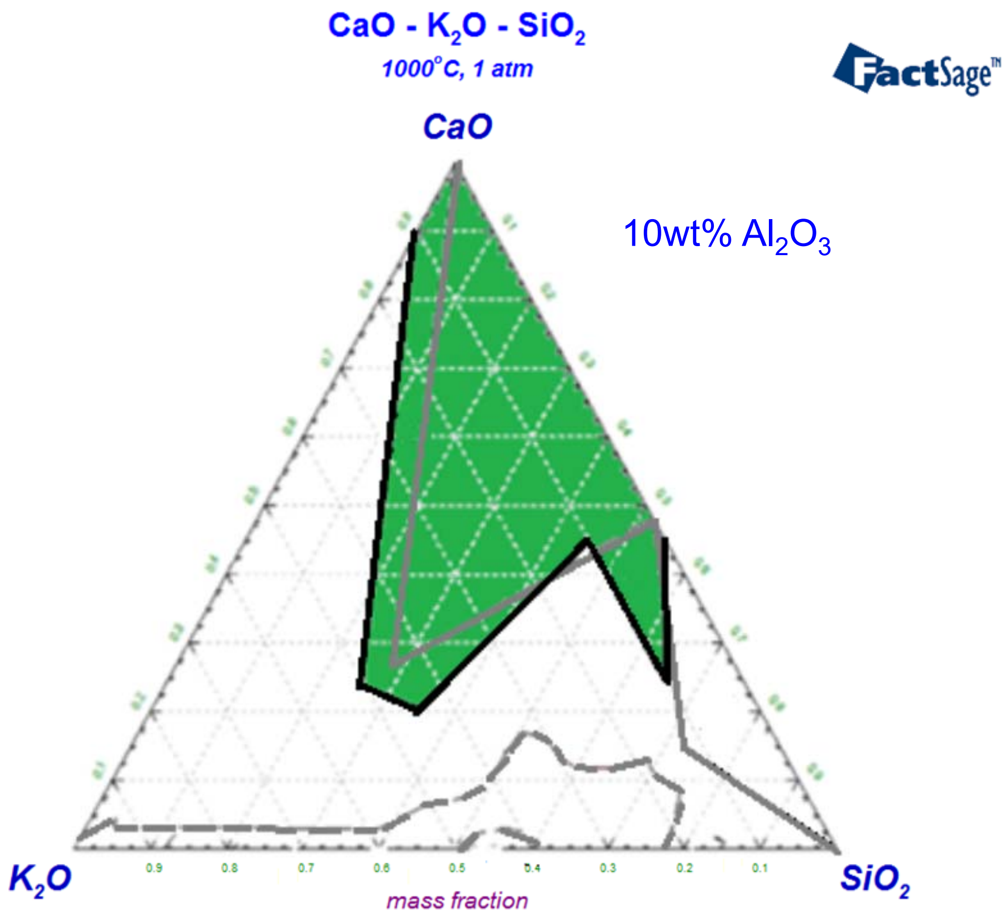
SIMPLIFIED TOOL TO CHARACTERIZE BIOMASS/WASTE

- **Quaternary diagram**
  - 4th oxide Al_2O_3

$$\frac{Al_2O_3}{CaO + K_2O + SiO_2} = 0.\bar{1}$$

- **Positive effect of Al_2O_3**
  - Solid domain increases
  - Liquid domain disapears

- **4th oxide calculated**
  - Al_2O_3, MgO, P_2O_5, FeO, SO_3



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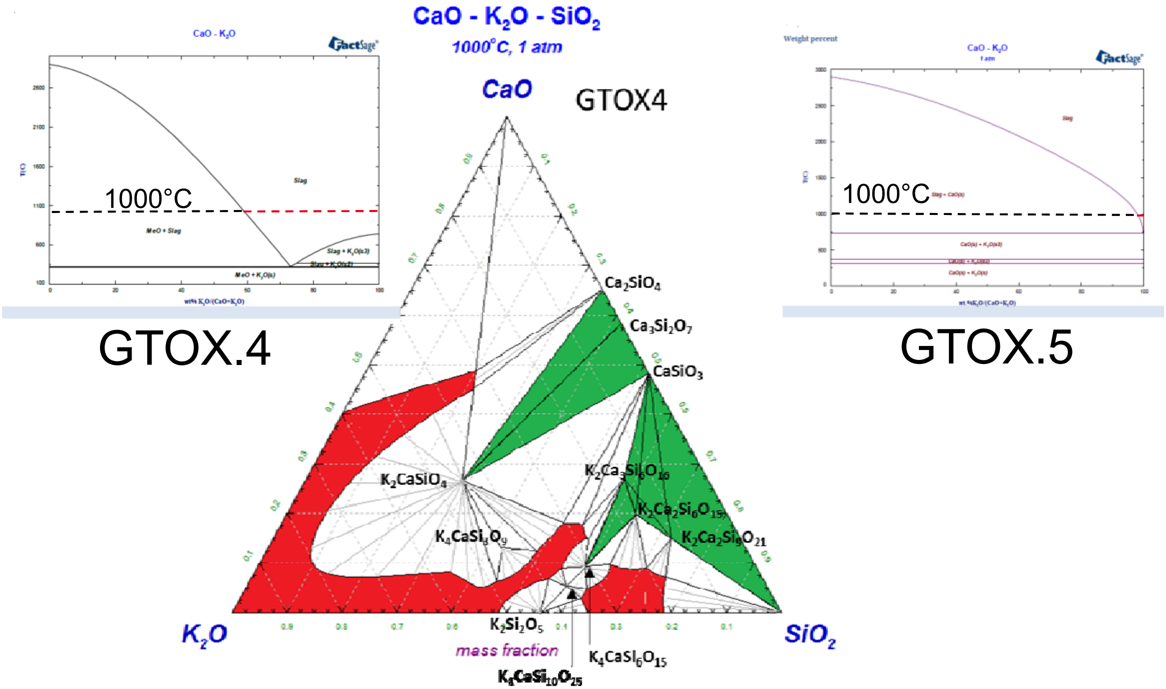
SIMPLIFIED TOOL TO CHARACTERIZE BIOMASS/WASTE

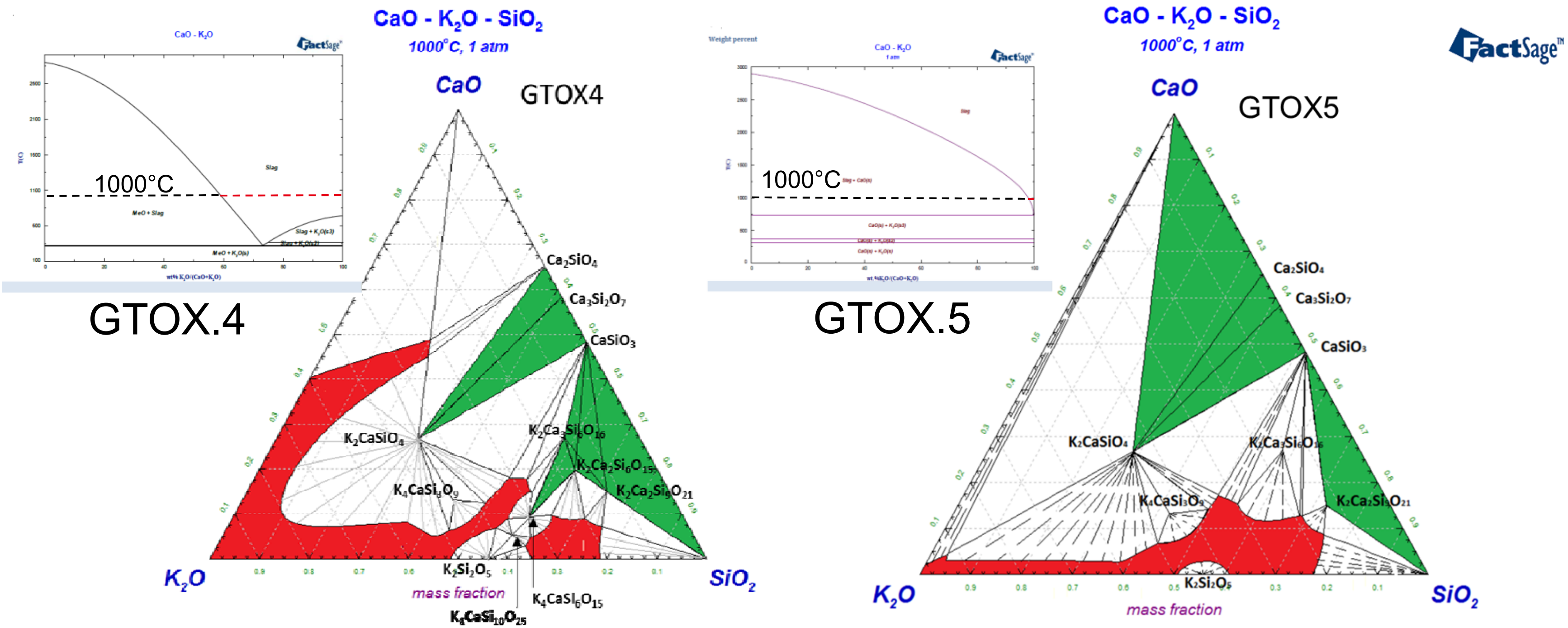
- **Strong uncertainty in key ternary phase diagram (CaO-K_2O-SiO_2)**



  - No data in CaO-K_2O (2 hypothesis GTOX4 → GTOX5)

SIMPLIFIED TOOL TO CHARACTERIZE BIOMASS/WASTE

- **Strong uncertainty in key ternary phase diagram (CaO-K_2O-SiO_2)**



- No data in CaO-K_2O (2 hypothesis GTOX4 → GTOX5)
- Existence of some ternary compounds not confirmed by recent literrature
- No data in many ternary compounds

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CONCLUSIONS

Thermodynamic equilibrium calculation in thermal conversion of biomass

- Now widely used in literrature to study the behavior of inorganic matter
- For biomass volatilisation
  - Need solution database for speciation
  - Experimental evidence for the alkali speciation
  - Kinetic limitation
- For ash behaviour (liquid phase)
  - Quite good agreement with calculation with GTOX.4 for silica rich biomass
- A new tool is proposed based on simplified draws of phase diagram
  - To predict biomass-process compatibility
- Strong uncertainties for silica poor biomass
  - Need experimental data for database developpers

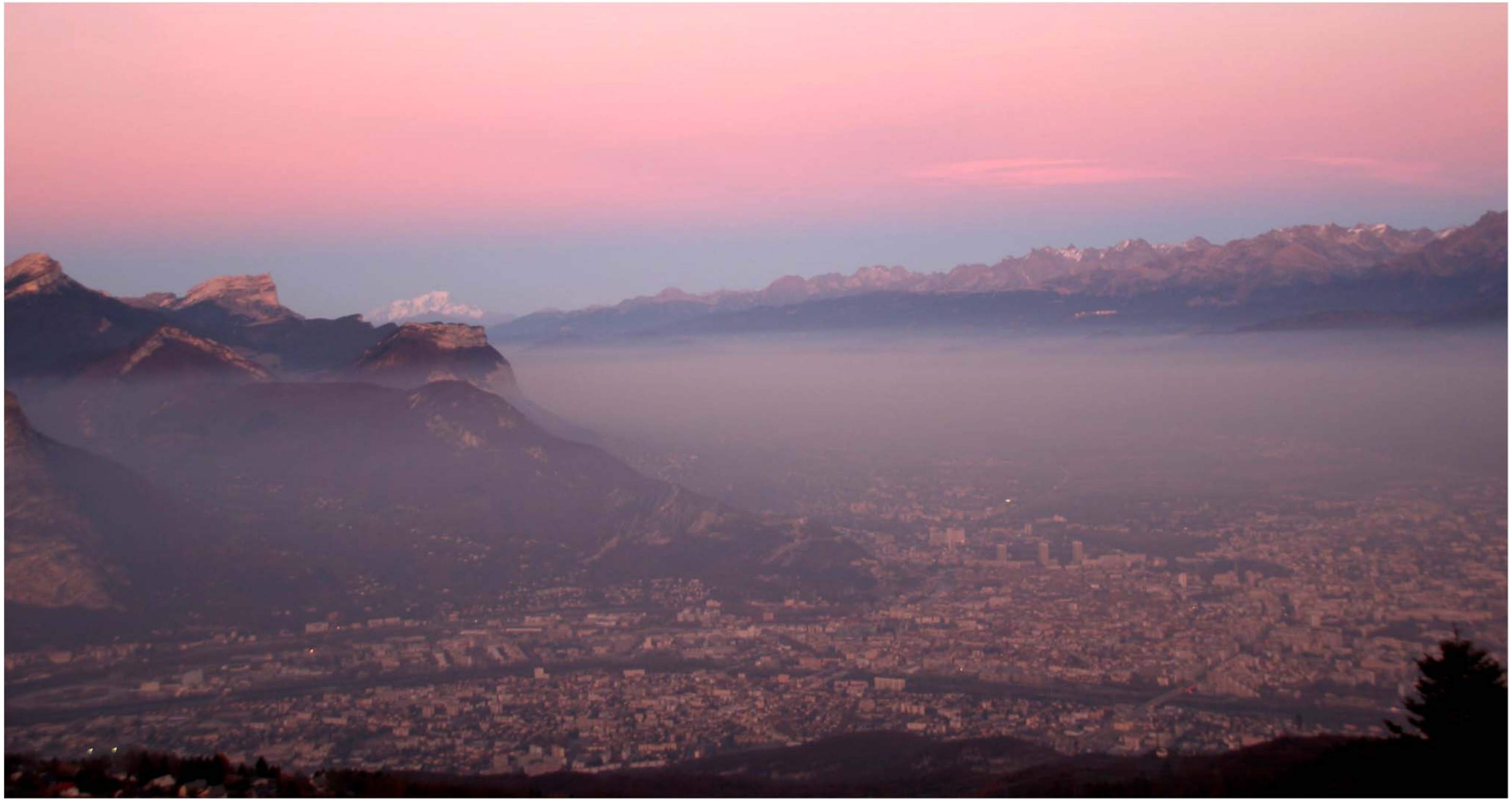
CONCLUSIONS

- **Future**

  - New calculations with GTOX.5 (phosphate compounds and solutions)
    - Need to select solutions (software <40 solutions)
    - Size of liquid description LIOS (software < ??)
    - Sulphur/sulphate included but what about with FTsalt carbonates, chloride salt?

  - Waste wood but thermodynamic database with solution missing
    - Coated particulate panel SiO_2-**TiO_2**-CaO + K_2O…(FTOxid but no TiO_2-K_2O)
    - Painted wood **BaO-TiO_2**-CaO (+**Zn**, Pb, K) no database
    - Impregnated wood **Cu-Cr-Ca-O** (K, As) no database

  - Simplified tool
    - Superposition of 3 quaternaries (3 temperatures or 3 compositions)
    - Validation on real cases (laboratory or pilot)



Thank you for your attention

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