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Bio Methanol Production via Chemical Looping Gasification Coupled with Membrane Reactors

Amir Soleimani Salim

Researcher at RISE Research Institute of Sweden

Adjunct Associate Professor at Chalmers University of Technology

Webinar:
Electrolysis and Gasification: possible synergies in energy and fuel production

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TECHNISCHE UNIVERSITÄT DARMSTADT



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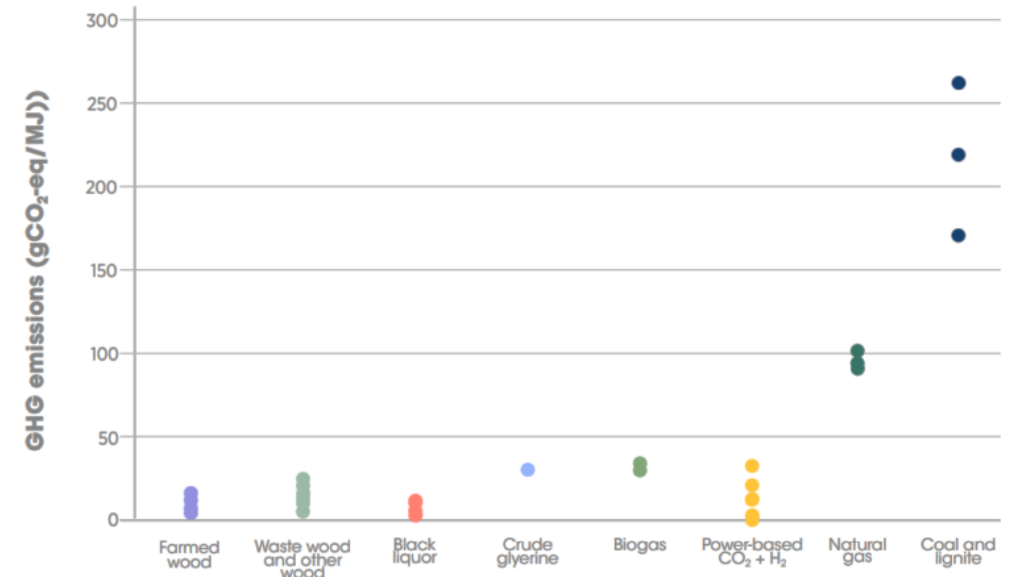
Swedish Environmental Research Institute



Methanol



- Besides being an important chemical commodity, methanol is a multipurpose fuel that can be used directly in internal combustion engines, blended with other fuels or for producing fuel additives.
- Methanol can be used both directly and indirectly for electricity production in fuel cells.
- In 2020, around 65% of methanol is produced by natural gas reforming, and 35% is produced by coal gasification. Only less than 1% of global methanol production is renewable methanol.
- Around 102 Mt of methanol were produced in 2020 with expectations of increasing to 500 Mt/year by 2050.
 - Correspond to releasing 1.5 Gt CO₂ per annum if solely sourced from fossil fuels.



GHG emission for methanol production from various feedstocks

Innovation Outlook: Renewable Methanol (2021), International Renewable Energy Agency (IRENA)



BioMethanol

- While the production of biomethanol from biomass can significantly reduce the CO₂ emission, the amounts of biomass that can be generated in a sustainable way are limited.
- Currently there are several on-going/operational projects for biomethanol production from MSW, and waste wood using gasification technologies
 - the overall conversion efficiency of the gasification technologies and methanol synthesis methods is low
 - the yield of biogenic carbon in the biomethanol product is relatively low
 - these technologies are often unable to utilize low-value biogenic residues without pretreatment as feedstock, owing to their heterogenous nature and naturally high amount of contaminants
- According to IRENA, the cost of biomethanol can increase significantly from \$43/ton to \$660/ton by increasing the cost of biomass (from 1.5 \$/GJ to 15 \$/GJ) and decreasing conversion efficiency (from 70% to 50%) and while the cost of fossil-based methanol is \$100-250/ton.

Innovation Outlook: Renewable Methanol (2021), International Renewable Energy Agency (IRENA)

- To meet the increasing global demand for methanol
- To meet the net zero emission by 2050
- To reduce the cost of biomethanol to facilitate the adoption and large-scale investments.

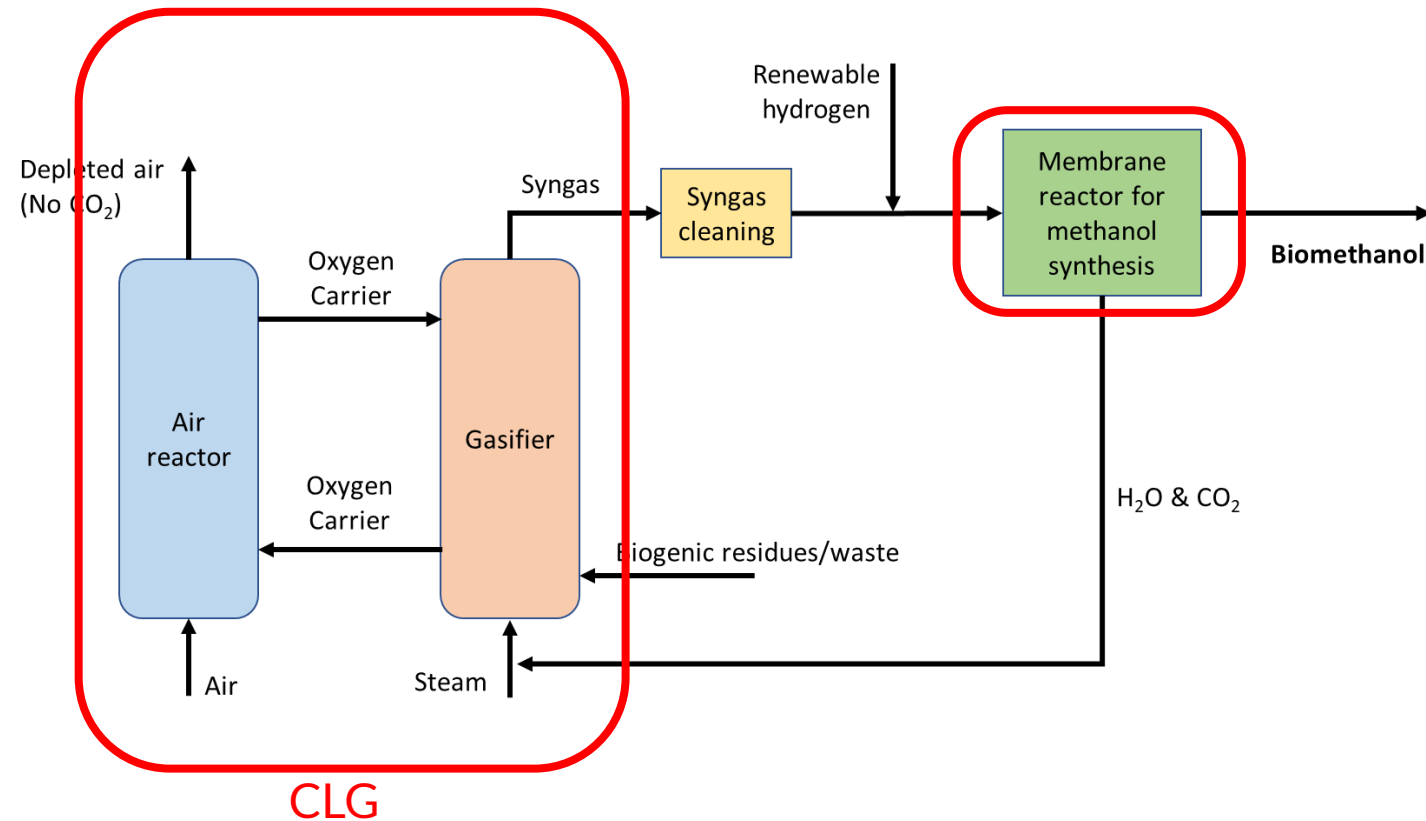
➤ It is necessary to develop **efficient processes** for the conversion of **low-value biogenic residues and waste** to **biomethanol**

Bio-MeGaFuel idea:

biomethanol production via chemical looping gasification (CLG) coupled with membrane reactors

Advantages:

- Flexible toward feedstocks and can utilize various biogenic residues and wastes
- Higher conversion efficiency compared to conventional gasification and methanol synthesis methods, leading to lower production costs and maximum biogenic conversion to biomethanol.
- Reducing the number of downstream units, with the possibility of heat and power integration, provides significant potential for cost and energy demand reduction.
- Produce biomethanol with near zero emissions (significant emission reduction).
- The process is less energy intensive and is self-sufficient in terms of heat.

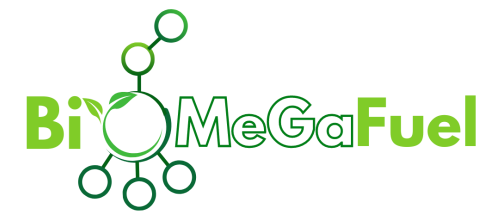


Bio-MeGaFuel Consortium

Duration: 48 months

Start date: September 2024

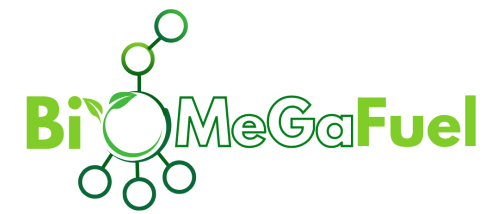
Budget: Approximately 3.8 Million Euros (Funded by EU)



| | Participant organisation name | Country |
|----|--|-------------|
| 1 | RISE RESEARCH INSTITUTE OF SWEDEN | Sweden |
| 2 | GIDARA ENERGY | Netherlands |
| 3 | G.I. Dynamics (Affiliated to GID) | Netherlands |
| 4 | TECHNISCHE UNIVERSITÄT DARMSTADT | Germany |
| 5 | EINDHOVEN UNIVERSITY OF TECHNOLOGY | Netherlands |
| 6 | SPANISH NATIONAL RESEARCH COUNCIL | Spain |
| 7 | IVL SWEDISH ENVIRONMENTAL RESEARCH INSTITUTE | Sweden |
| 8 | PERPETUAL NEXT BIOCARBON | Netherlands |
| 9 | 1CUBE | Netherlands |
| 10 | BLUE WORLD TECHNOLOGY | Denmark |



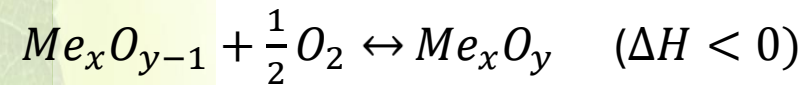
Technology development activities



| Activity | Bio-MeGaFuel TRL | Verification |
|--|------------------|--|
| CLG of low-value waste and biogenic residues to produce syngas | 5 | Gasification of 50-70 tons of low-value biogenic residues and waste in a 1 MW unit with: <ul style="list-style-type: none"> • >100 h autothermal CLG operation , • mixing using CO₂ and steam as the fluidizing and gasification agent, • 80% gasifier cold gas efficiency, • 98% carbon conversion in gasifier, • <10% of reactive ash species released in air reactor. |
| Methanol synthesis from syngas using a membrane reactor | 5 | Production of 3 kg/day of biomethanol with a double yield of methanol production from syngas compared to packed beds and with in-situ CO ₂ separation. |

Chemical looping gasification

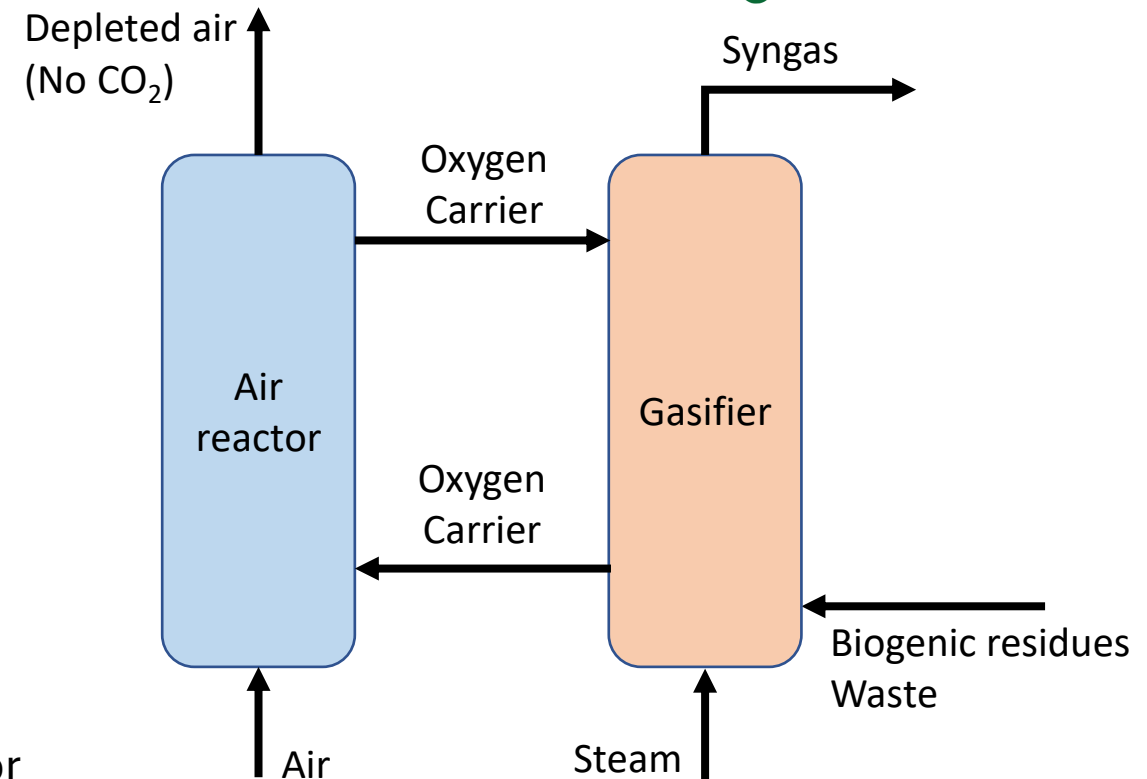
Oxygen carrier (OC):



Me_xO_y : Metal (such as Fe, Mn, Cu or Ni) oxides particles in the range of 100–500 μm

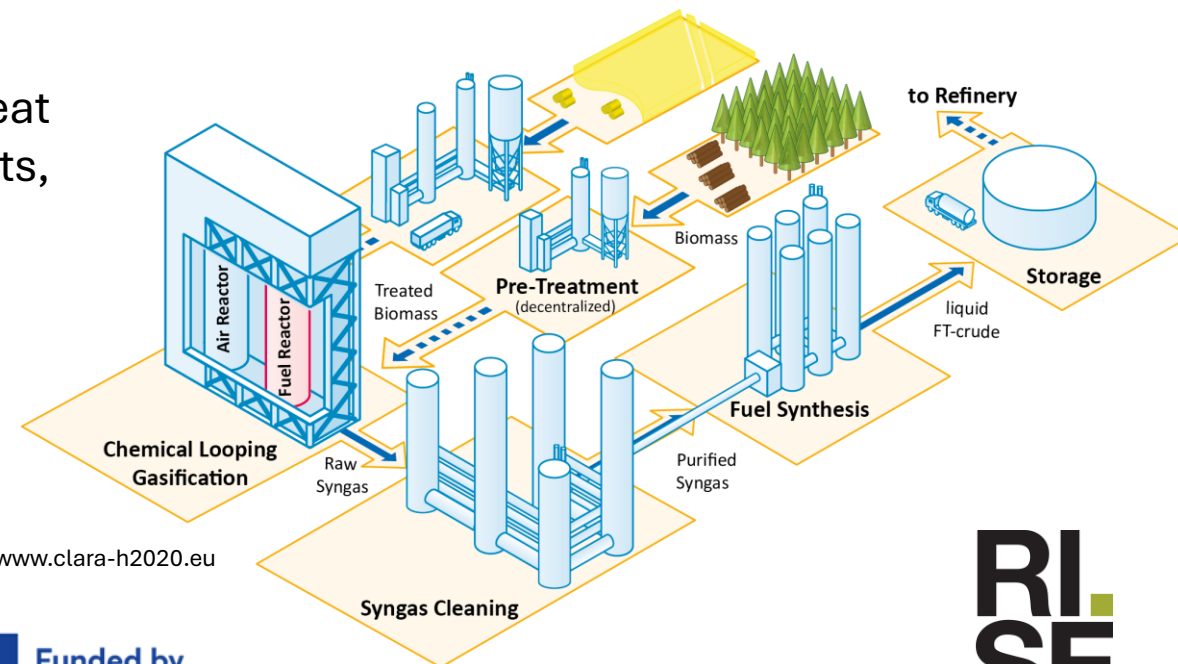
OC can be:

- natural ores such as ilmenite
- industrial waste materials such steel slag convertor and copper slag
- Synthetic material such as pervoskites



Chemical looping gasification

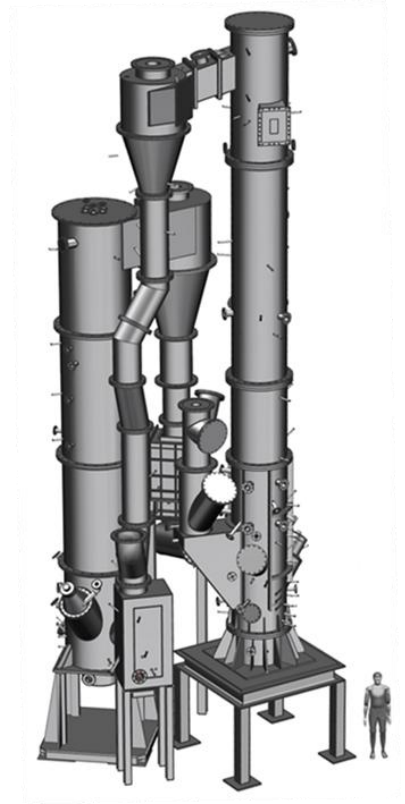
- No Nitrogen Dilution Compared to Air Gasification
 - Higher calorific value of the syngas, and less CAPEX and OPEX for syngas cleaning.
 - The produced CO₂ in the syngas is concentrated, meaning that CO₂ can be removed with low energy penalty
- No Need for Pure Oxygen
 - No ASU → Less energy penalty and CAPEX, and higher energy efficient
- The oxygen carrier promotes uniform heat distribution and reduces local hotspots, enhancing overall reaction stability.



CLARA H2020 “CHEMICAL LOOPING GASIFICATION FOR SUSTAINABLE PRODUCTION OF BIOFUEL”, www.clara-h2020.eu

Chemical looping gasification

- Improved Syngas Quality
 - CLG typically produces syngas with a higher H_2/CO ratio,
 - desirable for: Fischer–Tropsch synthesis, Methanol production, Hydrogen generation, etc.
 - Lower Tar and Pollutant Formation
 - The presence of oxygen carriers promotes tar cracking and reforming reactions → Lower tar content and reduced sulfur and nitrogen pollutants
 - This simplifies downstream gas cleaning systems and lowers operational costs.
- Autothermal Operation
 - The process is self-sustaining in heat balance:
 - The oxidation of the metal oxide (in the air reactor) generates heat.
 - That heat is transferred to the fuel reactor (endothermic), maintaining desired temperatures without external fuel combustion.



1 MW unit at TU Darmstadt

Chemical looping gasification

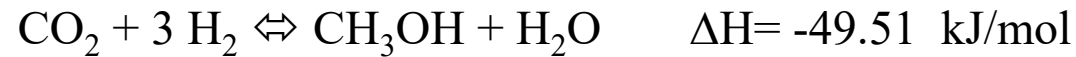
- Higher Carbon Conversion, syngas yield and Fuel Flexibility
 - CLG provides a more controlled oxidation environment, improving:
 - Carbon conversion efficiency (less unreacted char)
 - Syngas yield (less unreacted char and tar)
 - Fuel flexibility, allowing the use of difficult biomass, or waste-derived fuels as feedstock

| Technology | Gasifying Agent | Cold Gas Efficiency (CGE) | Carbon Conversion | Overall Energy Efficiency |
|--|---------------------|---------------------------|-------------------|---------------------------|
| Air Gasification | Air | 55–70% | 85–95% | 50–60% |
| Steam Gasification | Steam | 60–75% | 85–98% | 55–65% |
| Oxygen Gasification | O ₂ | 70–80% | 95–99% | 60–70% |
| Chemical Looping Gasification (CLG) | Metal oxide + Steam | 80–90% | 98–100% | 70–85% |

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Methanol synthesis via membrane reactors

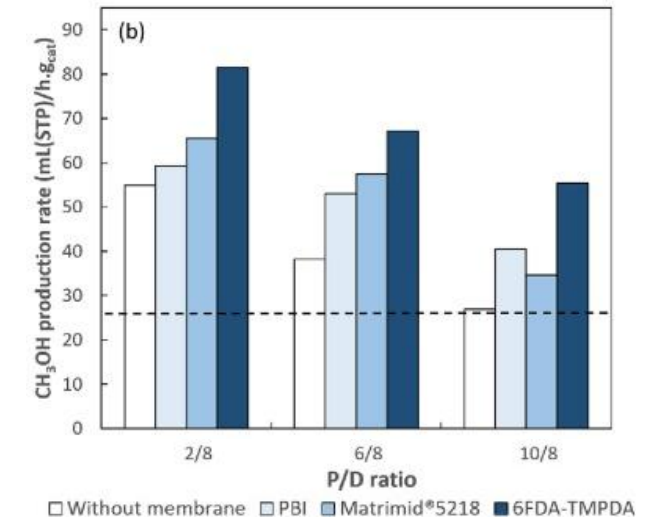
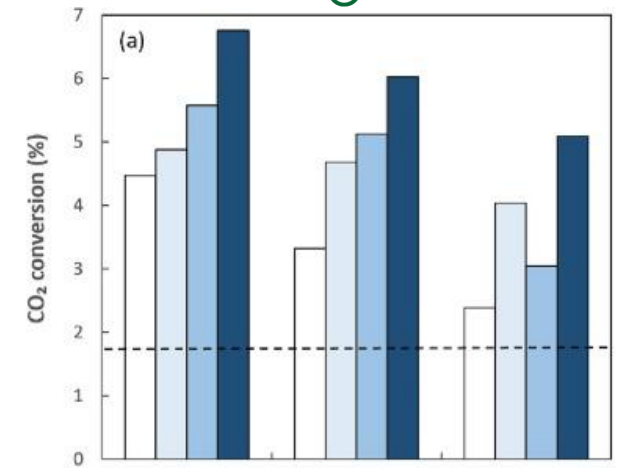
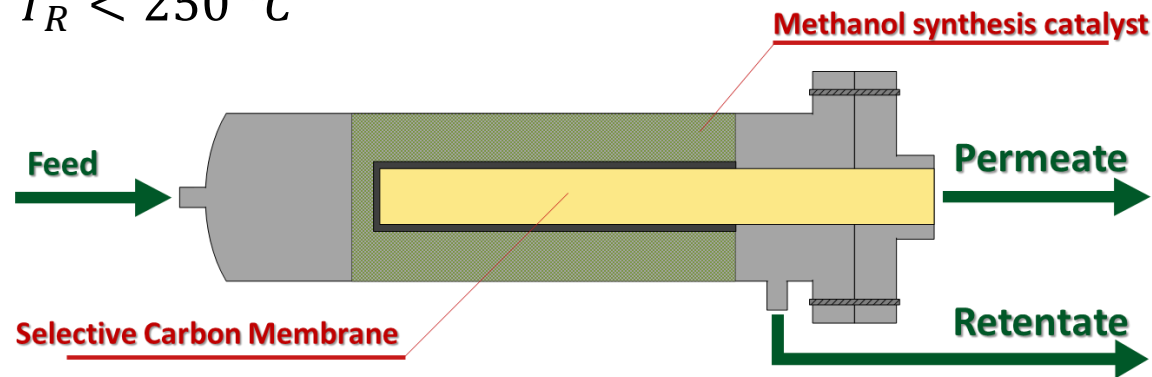
The methanol synthesis is an equilibrium system:



Commercial Cu/ZnO/Al₂O₃ catalyst

$$P_R < 40 \text{ bar}$$

$$T_R < 250 \text{ }^\circ\text{C}$$



Pham et al., *Chem. Eng. J.* 2024, 489, 151442
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Thank you for your attention



LinkedIn



Amir Soleimani Salim (amir.soleimani.salim@ri.se)

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