Catalytic Treatments of Biomass Derived Gas I

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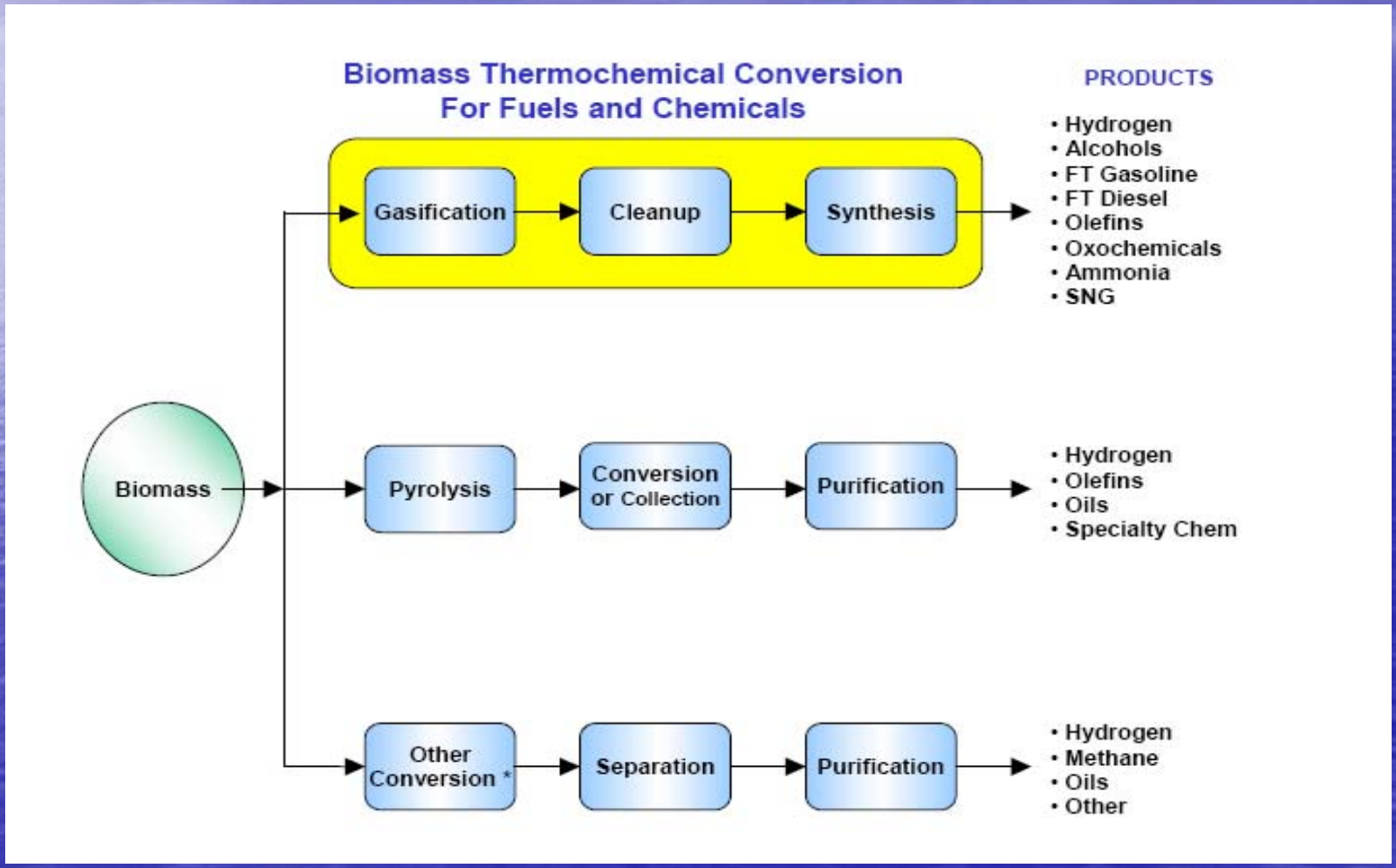
Utilization of Biomass

- Terpenes
- Drugs& Agro Chemicals
- CHEMICALS
- Levoglucosan
- Phenolics
- Pyrolysis Oils
- FUELS
- Ethanol
- Liquid & Gaseous Fuels
- Protein Polymeric Materials
- Starch Polymeric Materials & Chemicals
- Lignocellulosic Composites
- Plastics
- MATERIALS
- Cellulosic Polymers
- Linear Polyurethanes &Polyesters
- Light& Low MW Rubber
- Soybean Printing Inks
- Nylons
- FATS &OILS
- Automobile Fluids
- Solvents For Coatings

Thermochemical Conversion of Biomass



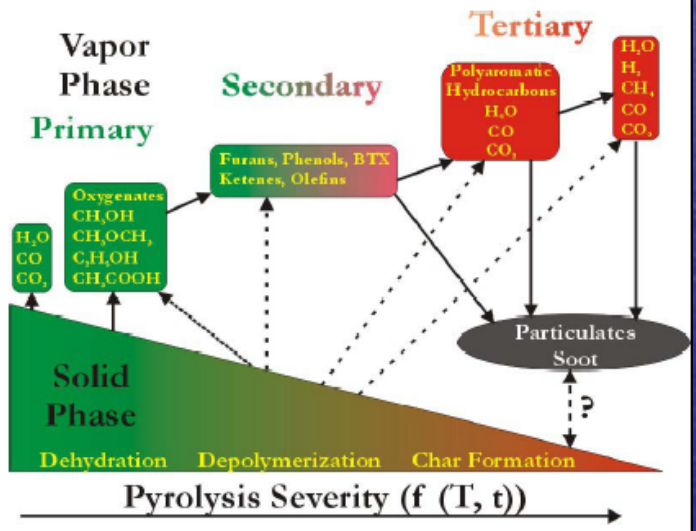
Basic Definitions

Pyrolysis

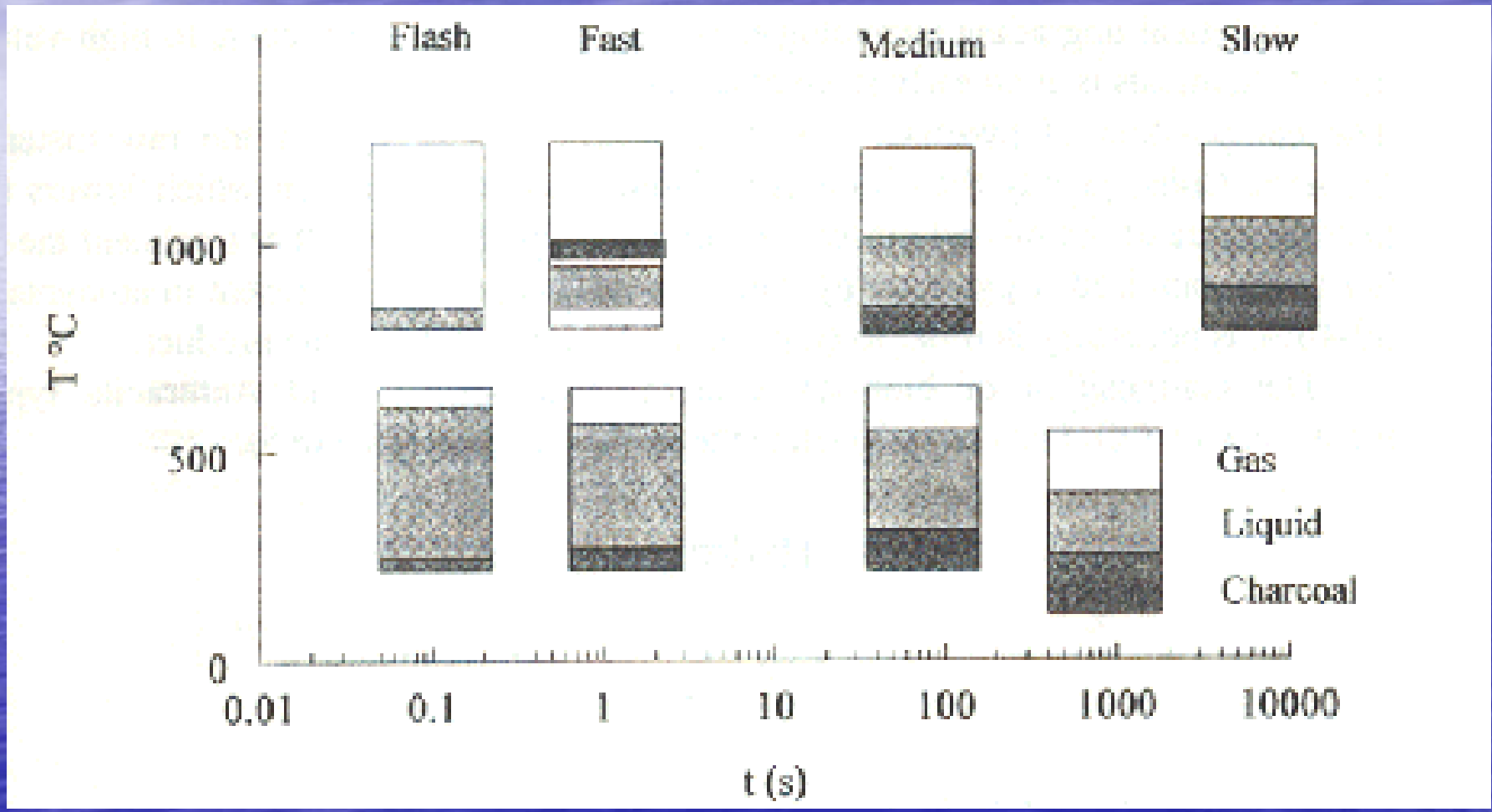
- Thermal conversion (destruction) of organics in the absence of oxygen
- In the biomass community, this commonly refers to lower temperature thermal processes producing liquids as the primary product
- Possibility of chemical and food byproducts

Gasification

- Thermal conversion of organic materials at elevated temperature and reducing conditions to produce primarily permanent gases (CO, H2, CH4, etc.), with char, water, and condensibles as minor products
- Primary categories are partial oxidation and indirect heating



Classification of Pyrolysis



Methods to Remove Tars from Producer Gas

- **Physical Process**
  - **Filters, Wet Scrubbers**
- **Thermal Process**
  - **Temperature exceeding 1000^{o}C**
  - **require expensive alloys**
- **Catalytic Process**
  - **Operate at much lower temperature (600-800^{o}C) than thermal process**
  - **Provide the simplest and most effective means of removing tar**

Tar Decomposition Reaction

- Cracking
  - $pC_nH_x \rightarrow qC_mH_y + rH_2$
- Steam Reforming
  - $C_nH_x + nH_2O \rightarrow (n+x/2)H_2 + nCO$
- Dry Reforming
  - $C_nH_x + nCO_2 \rightarrow (x/2)H_2 + 2nCO$
- Carbon Formation
  - $C_nH_x \rightarrow nC + x/2\ H_2$

Criteria for the Catalyst

- The catalysts must be effective in the removal of tars
- If the desired product is syngas, the catalysts must be capable of reforming methane
- The catalysts should provide a suitable syngas ratio for the intended process
- The catalysts should be resistant to deactivation as a result of carbon fouling and sintering
- The catalysts should be easily regenerated
- The catalysts should be strong
- The catalysts should be inexpensive

Two Distinct Groups of Catalyst

- Primary Catalyst

  -added directly to the biomass prior to gasification

  - addition is either by wet impregnation of the biomass material or by dry mixing of the catalyst

  - purpose is reducing the tar content and have little effect on the conversin of methane and C2-3 hydrocarbons in the product gas

  - operate under the same conditions of the gasifier

Two Distinct Groups of Catalyst

- Observation with Primary Catalyst
  - A change in product distribution
  - A decrease in tar amount
  - an increase in hydrocarbon production
  - a slight decrease in the amount of CO and increase in the amount of CO2
  - an almost no variation in the amount of CH4
  - Problems regarding catalyst deactivation and carryover of fines were severe
  - Catalytic tar reduction depends on gasification conditions

Catalyst in primary measures

Table 1
In-bed additives used by researchers under different operating conditions

Feed	Feed properties		Operating conditions			Additive	Reference
	Moisture (%)	Size (mm)	Gasif. agent	Temp (°C)	Time (s)		
Cellulose	—	1.0–2.0	Steam	600–800	1.26–1.54	Limestone	Walawender et al. [33]
Wood	—	—	Steam	750	—	K_2CO_3	Douglas et al. [52]
Pine sawdust	8.5	1.0	Steam	750	—	Dolomite FCC	Corella et al. [37]
Pine sawdust	10–25	−4.0–0.8	Air	800	0.6	Dolomite	Narváez et al. [13]
Pine chips	10–12	−5.0–1.0	Steam/O_2	795–835	—	Dolomite	Olivares et al. [38]
Pine sawdust	10	—	Steam	700	< 0.4	Ni–Al	Bilbao et al. [46]
Pine sawdust	10	—	CO_2	700	—	Ni–Al	García et al. [23]
Pine chips	—	—	Air;steam/O_2	800–850	—	Dolomite	Corella et al. [9]
Pine chips	10–15	—	Air	800–845	—	Dolomite FCC	Gil et al. [14]
Almond shell	7.9	1.1	Steam	770–820	—	Olivine Dolomite	Rapagnà et al. [39]
Birch	6–8	1.0–3.0	O_2–N_2	700–900	—	Silver sand Olivine	Rosén et al. [41]
Pine/bagasse	—	—	Steam	750	30	Ni-based	Baker et al. [44]

Two Distinct Groups of Catalyst

- Secondary Catalyst
  - placed in a secondary reactor downstream from the gasifier
  - Independent of the type of gasifier
  - Operated under different conditions

Tar Reduction Concept

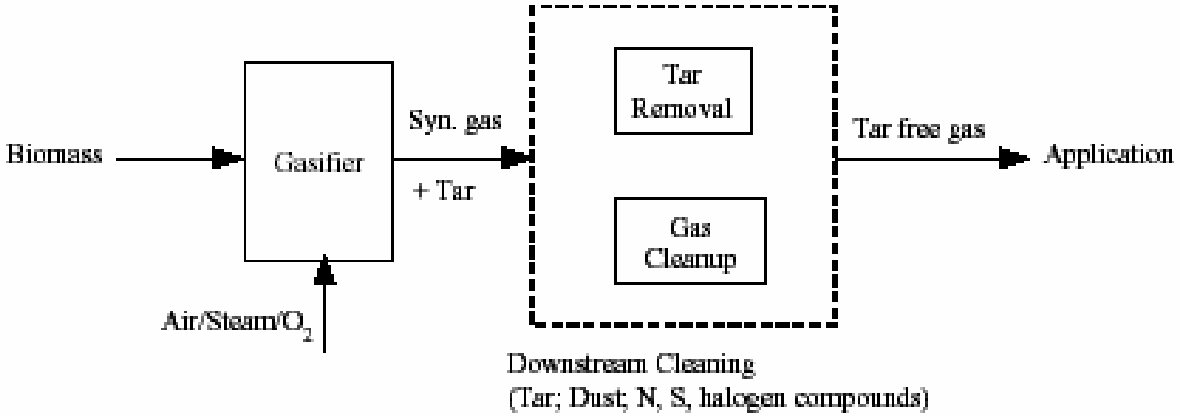


Fig. 1. Tar reduction concept by secondary methods.

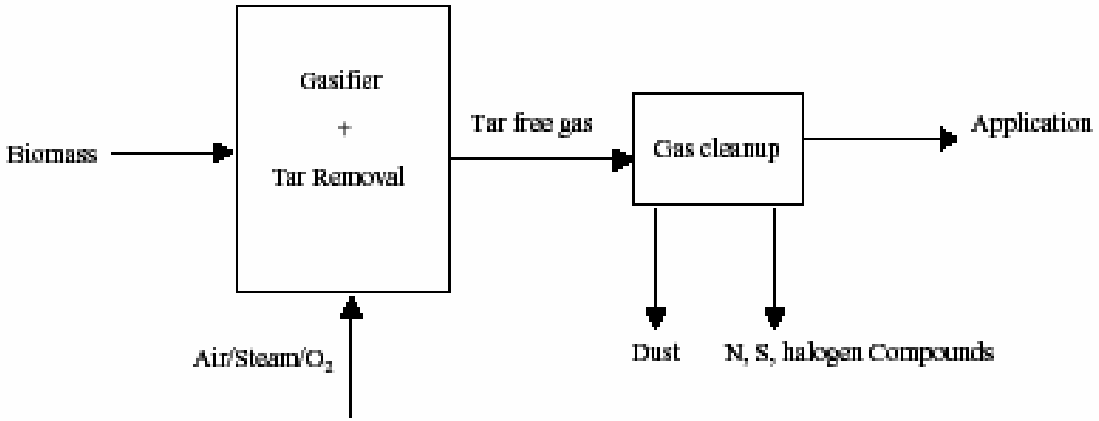


Fig. 2. Tar reduction concept by primary method.