Biomass 열분해

(Fast pyrolysis를 이용한 Bio-oil 생성을 중심으로)

서 울 시 립 대 학 교

박 영 권

발표내용 및 순서

I. Biomass의 잠재성

II. 대표적인 Biomass 열분해기술

III. Fast pyrolysis

IV. Bio-oil의 특징

V. Bio-oil의 활용

I. Biomass의 잠재성

- 에너지 저장물질
  - 광합성에 의한 태양에너지 저장물질
  - Renewable energy
- Non-fossil Chemical Feedstock
  - 다양한 유기화학물질 함유
- 환경에 대한 긍정적 효과
  - CO_2 흡수에 따른 Greenhouse-effect 저감효과

I. Biomass의 잠재성

- Biomass의 에너지(물질) 전환기술

Bio-chemical 전환

- 대표적 공정 : 발효, 혐기성소화 공정
- 생 산 물 질 : 알코올류, 아세트산류, 메탄가스 등

Thermo-chemical전환

- 직접연소(Combustion) : 열 회수
- 가스화(gasification) : 합성가스(CO, H2)
- 열 분 해 (pyrolysis) : 고/액/기체 형태의 연료회수

(*공정조건에 따라 분포율과 성분조절*)

II. 대표적인 Biomass 열분해 기술

- liquid fuel 생성목적을 중심으로...

Hydrous Pyroysis	Supercritical State of Steam (100~200bar)
Flash Pyroysis	Extremely Short Residence time
Hydro Pyroysis	Sufficient H_2 (100 bar)
Indirect Route	Gasification Gas cond.+ Fisher Tropsch cat

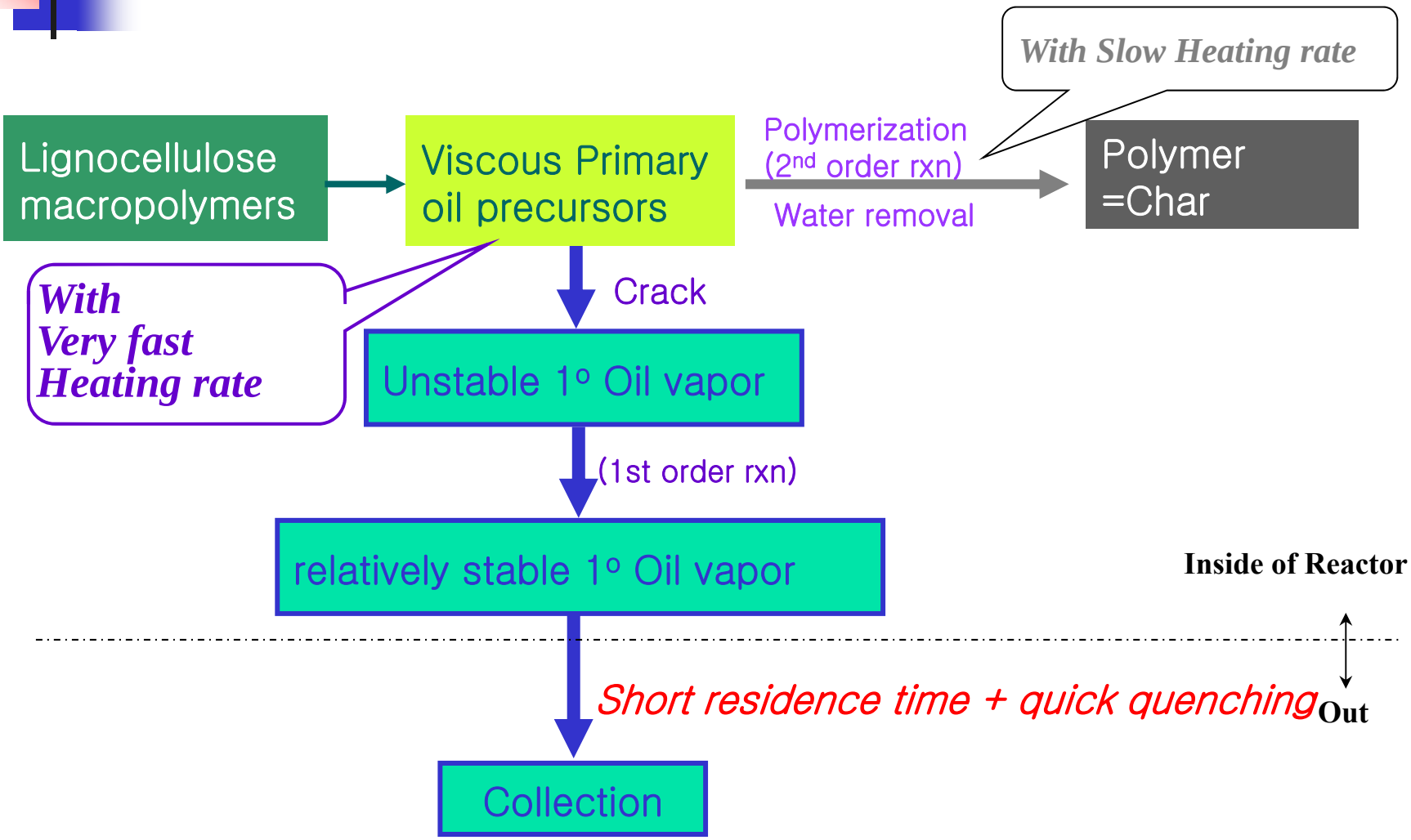
II. 대표적인 Biomass 열분해 기술

- liquid fuel 생성목적을 중심으로...

공 정	공 정 조 건	생성물 특징
Hydrous	- close to supercritical state of steam - high pressure(10~200 bar) - 340~360℃ - residence time 6~72hour - homogeneous catalyst	- low oxygen content - 50%이상 수분함량을 가진 시료에 적합
Flash	- 500~540℃ - extremely short residence time (preferably below 1sec)	- 산소함량 약 35~40% - 전통적인 연료와 섞이지 않음 - 수율 약75%(ash free, dry base) - 화학원료물질로 활용
Hydro-	- 풍부한 수소 - 약 100bar 정도의 압력 - 체류시간 1~30sec정도 범위 - 건조한 biomass	- space-time relationship 적다. - 산소함량이 낮다 - 전통적인 유류와 섞일 수 있다.
Indirect Route	gasification 합성가스를 Gas conditioning +Fisher Tropsch catalyst 이용하여 liquid synthesis 하는 방법	coke formation 최소화가 어려움

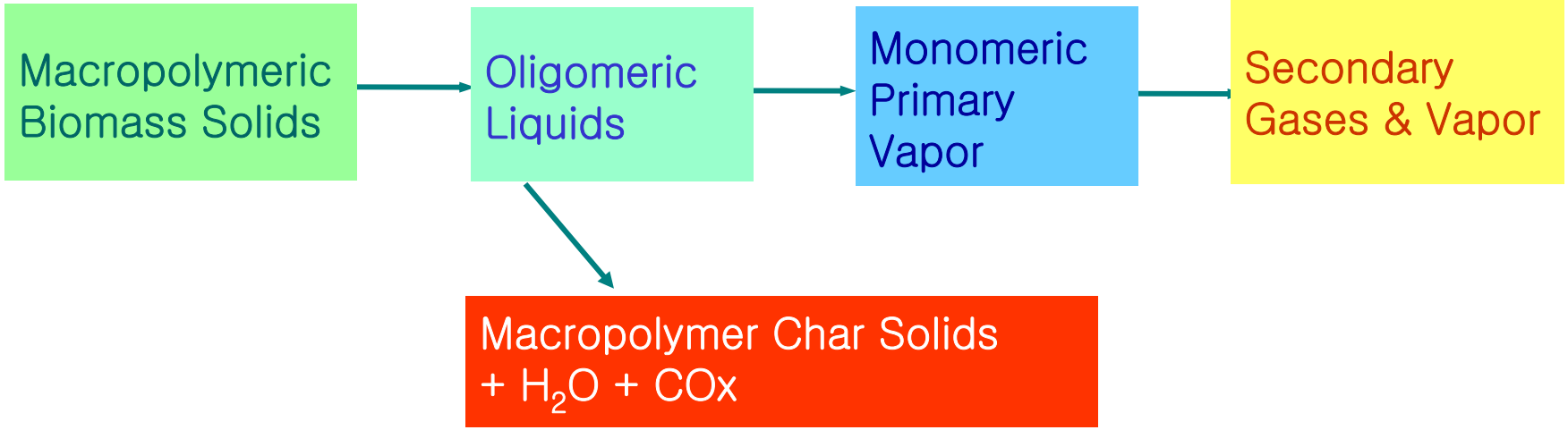
III. Fast Pyrolysis

- Heating rate에 따른 Biomass의 열분해



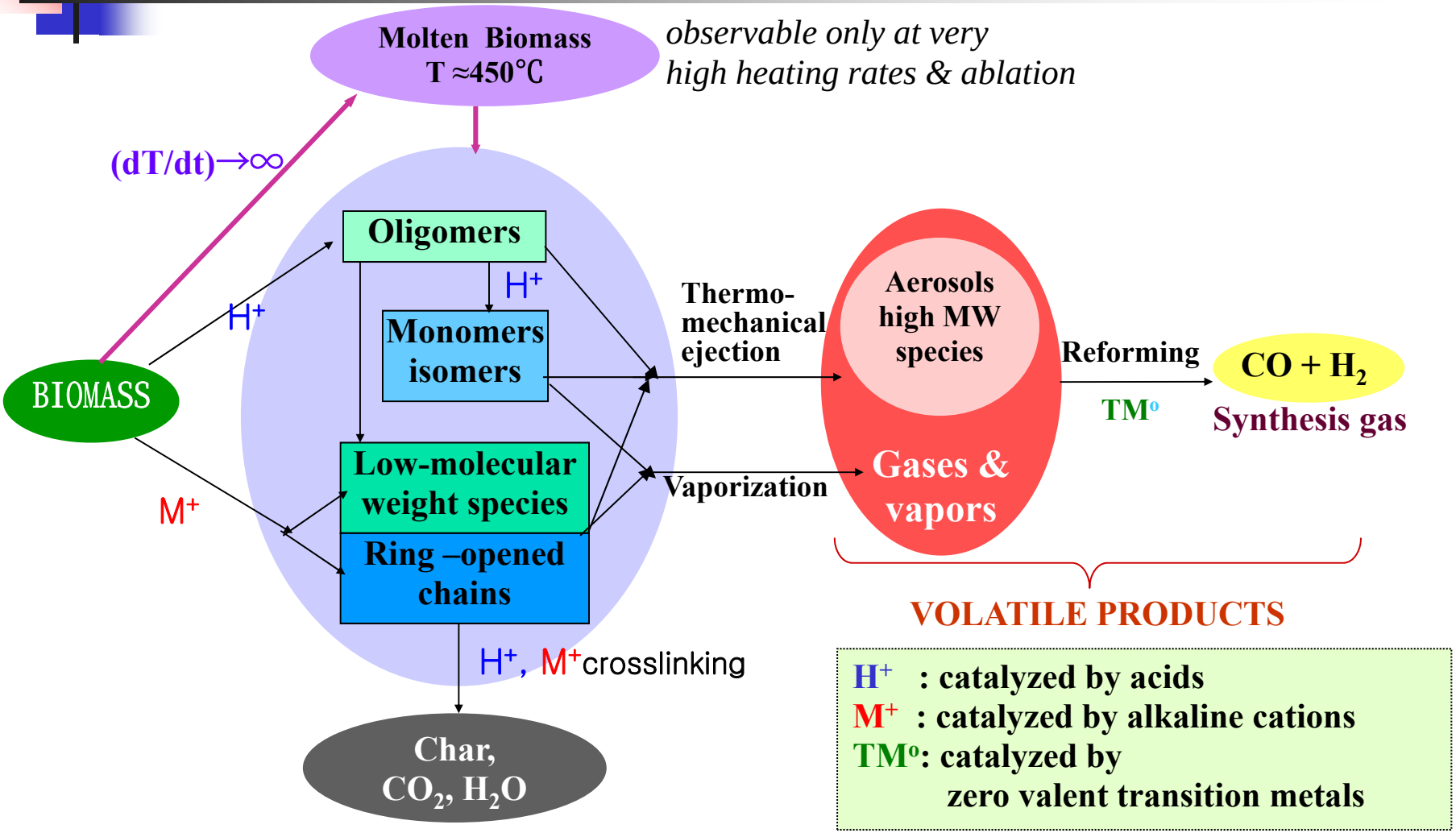
III. Fast Pyrolysis

- Fast pyrolysis의 Gloval Reactiom



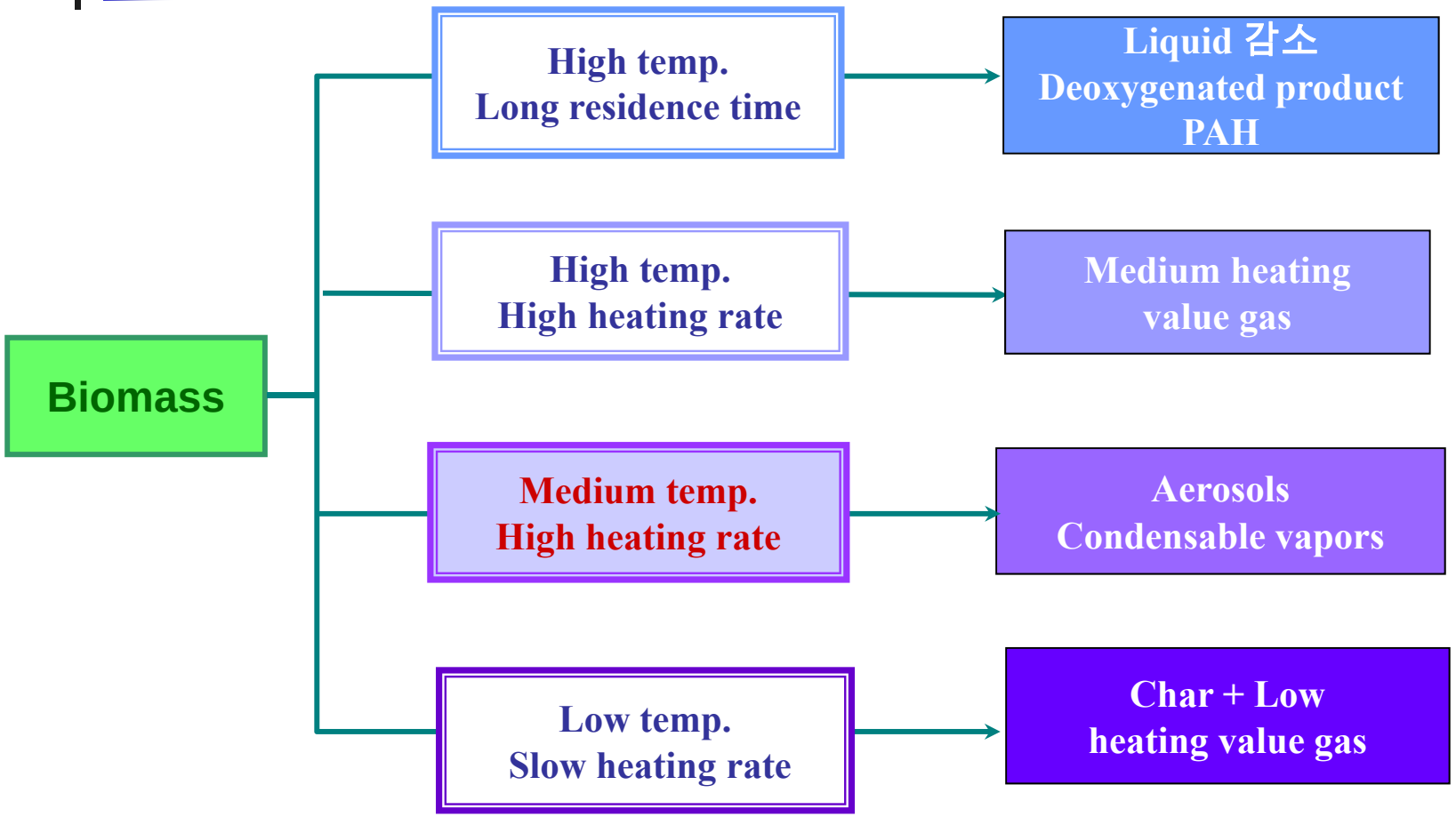
III. Fast Pyrolysis

- Mecanism of Biomass Pyrolysis...



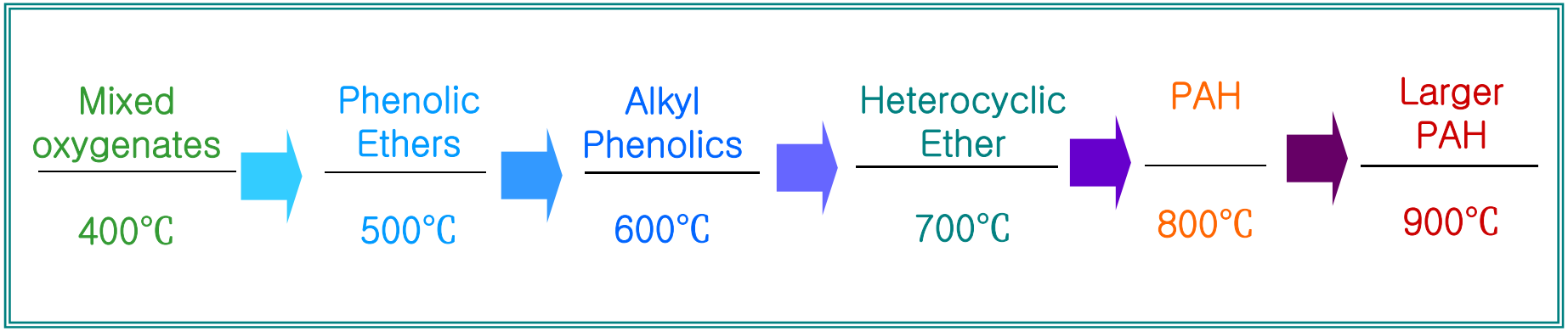
III. Fast Pyrolysis

-온도, 체류시간, 승온속도에 따른 생성물의 형태



III. Fast Pyrolysis

-Primary oil의 온도에 따른 전환 (Short residence time조건에서 ..)



고온으로 진행될 때 촉진되는 반응

- Dehydrogenation
- Condensation(aromatization)
- Dealkylation
- Deoxygenation

III. Fast pyrolysis

– 기술적 요구사항

공정상의 요구사항

- Heat Transfer ; Reactor configuration
- Heat Supply
- Feed preparation
- Ttemperature of reaction
- Vapor residence time
- Secondary vapor cracking
- Liquid collection
- Char separation
- Ash separation

반응기 고안 핵심 조건

- High heating rates
- Moderate temperatures
- Short vapor product residence time 조건

* *char와의 접촉 최소화*

III. Fast pyrolysis

-Reactor configuration (1)

Reactor type	Suggested mode of heat transfer	Advantages/ Disadvantages/Features
Ablative	95% Conduction 4% Convection 1% Radiation	•Accepts large size feedstocks •Very high mechnical char abrasion from Biomass •Compact design •Heat transfer problematical •Particlate transport gas not always required
Circulating Fluid bed	80% Conduction 19% Convection 1% Radiation	•High heat transfer rate •High char abrasion from biomass and char erosion •leading to high char in product •Char/solid heat carrier separation required •Solids recycle required : Increased complexity of system •Maximum particle size up to 6mm •Possible liquids cracking by hot char •Possible catalytic activity from hot char •Greater reactor wear possible

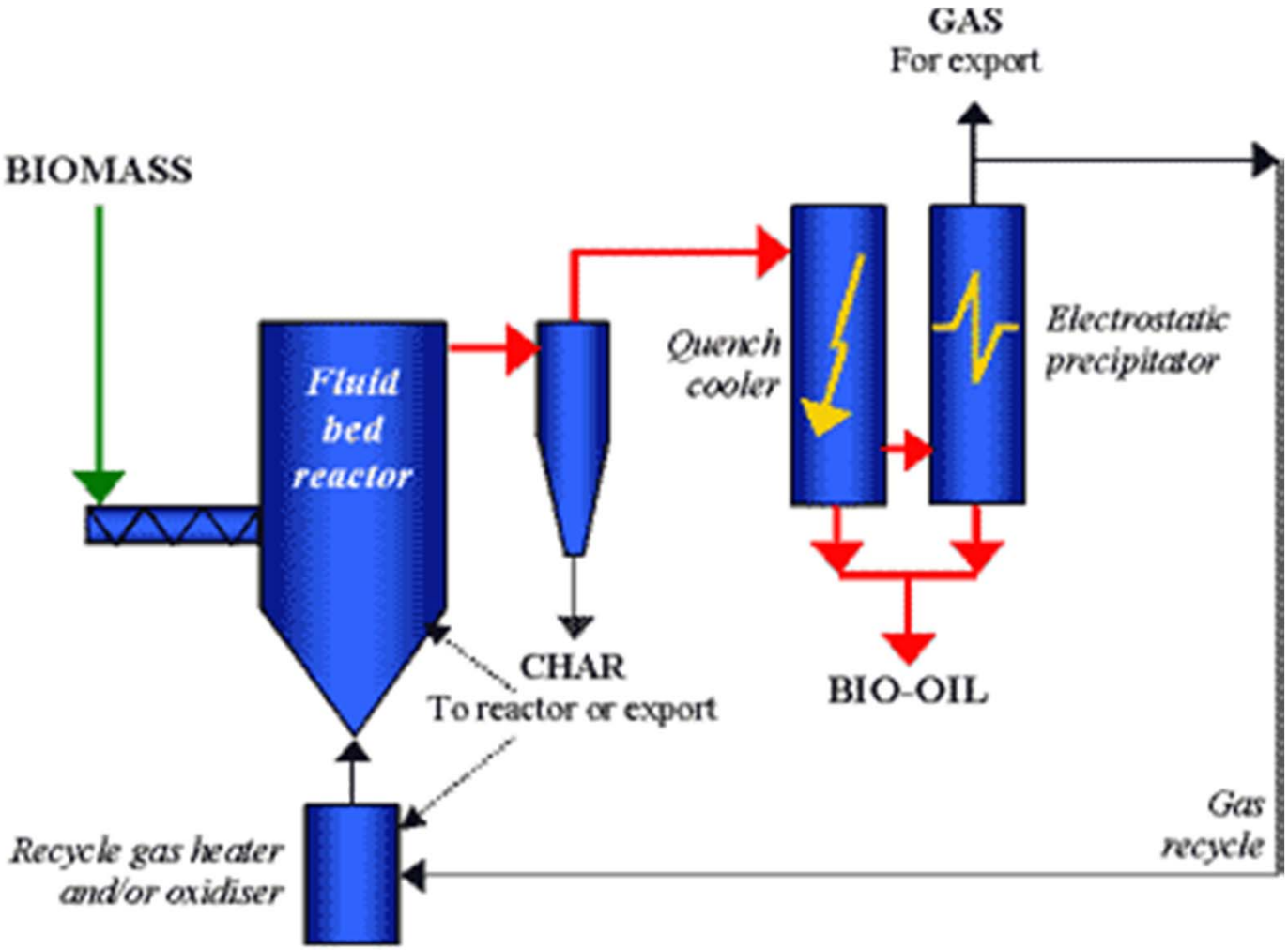
III. Fast pyrolysis

-Reactor configuration (2)

Reactor type	Suggested mode of heat transfer	Advantages/ Disadvantages/Features
Fluid bed	90% Conduction 9% Convection **1% Radiation**	•High heat transfer rates •Heat supply to fluidizing gas or to bed directly •Limited char abrasion •Very good solid mixing •Particle size limit<2mmin smallest dimension •**Simple reactor configuration**
Entrained flow	4% Conduction 95% Convection **1% Radiation**	•Low heat transfer rate •Particle size limit<2mm •**Limited gas/solid mixing**

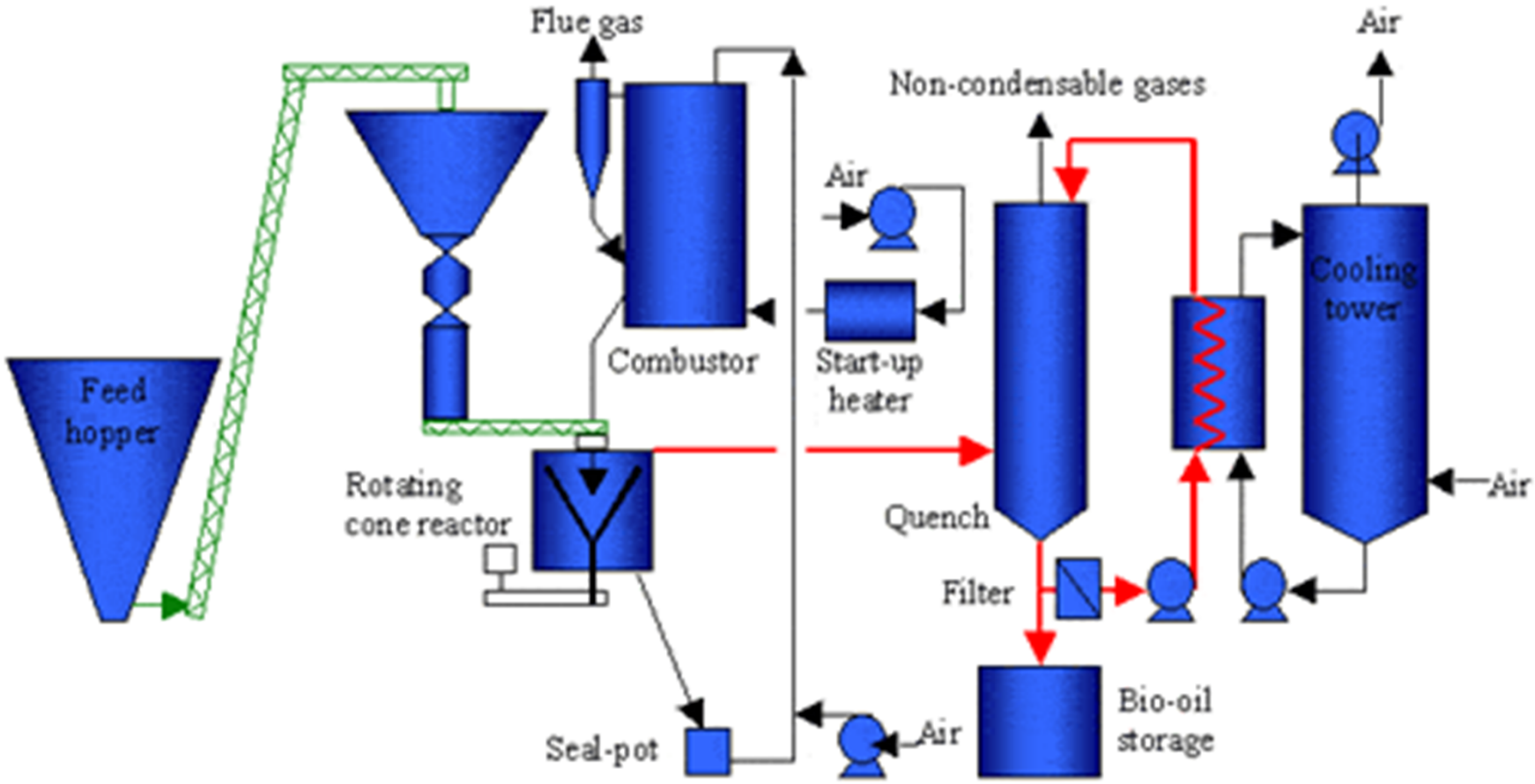
III. Fast pyrolysis

- Fludized bed Reactor Process



III. Fast pyrolysis

- Rotating Corn Reactor Process



Ⅳ. Bio-oil의 특성

- Characteristics

Bio-oil의 특성에 영향을 미치는 중요요소

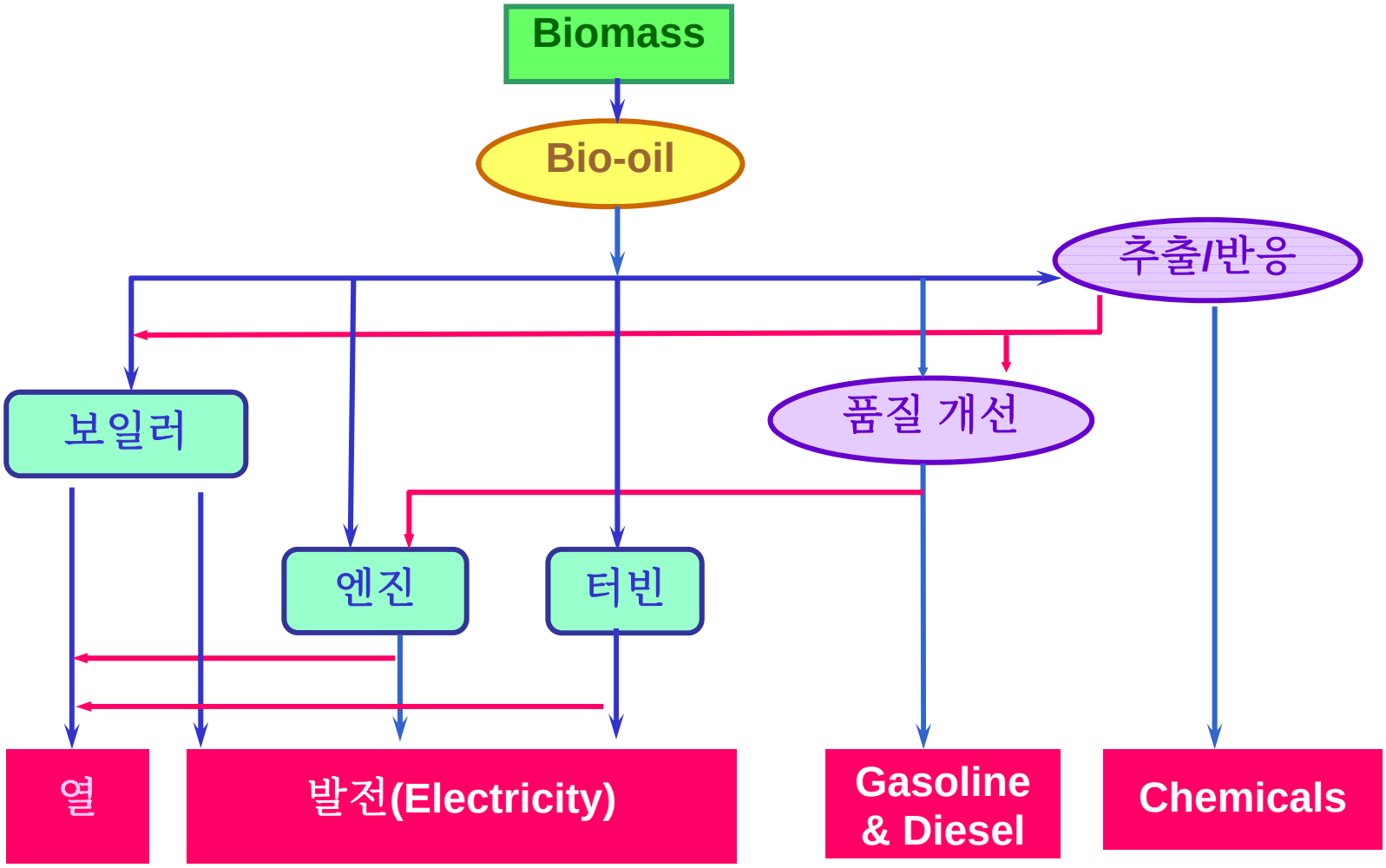
- Feed material의 특성
- Pyrolysis process parameters
- Liquid collection parameters
- 높은 산소함량
  - high viscosities
  - high boiling points
  - relatively poor chemical stability
  - hydrophilic character
    =mostly insoluble in hydrocarbon solvent

Ⅳ. Bio-oil의 특성
- Physical properities

Physical Properities	Typical Value
Moisture content	25%(15~30%)
specific gravity	1.20
HHV(moisture free basis)	22.5MJ/kg
HHV (depend on moisture)	17.0 MJ/kg (16~19 MJ/kg)
Viscosity (at 40℃)/ (at 40℃,25%water)	30~200cp / 40~100cp
Pour point	-23℃
pH	2.5
solids (char)	0.5%
Distillation	Max.50% as liquid degrades
C H N S Ash O (by different)	56.4% 6.2% 0.2% <0.01% 0.1% 37.1%

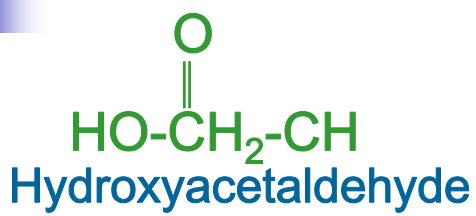
V. Bio-oil의 활용

- 일반적인 활용범위의 개요

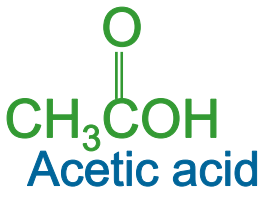


V. Bio-oil의 활용

-Ligno cellulosic feedstock으로부터 분리/추출/정제

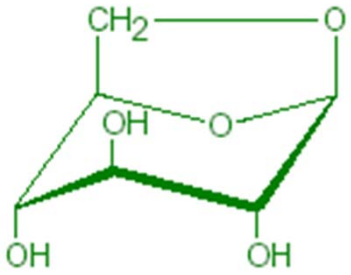


Hydroxyacetaldehyde

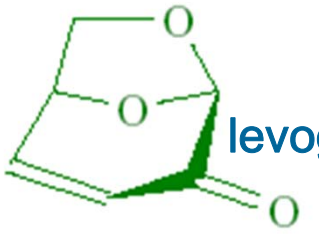


Acetic acid

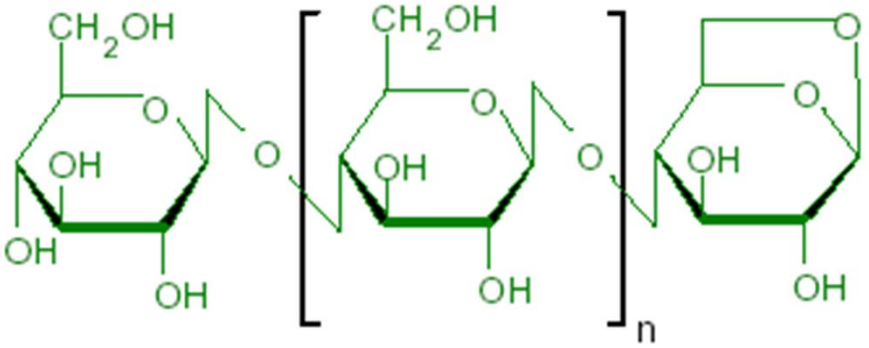
Formic acid



levoglucosan



levoglucosenone



Anhydro-oligosaccharudes

n=0 : Cellobisan

n=1 : Cellotriosan

V. Bio-oil의 활용

-Whole Bio-oil의 Utilization

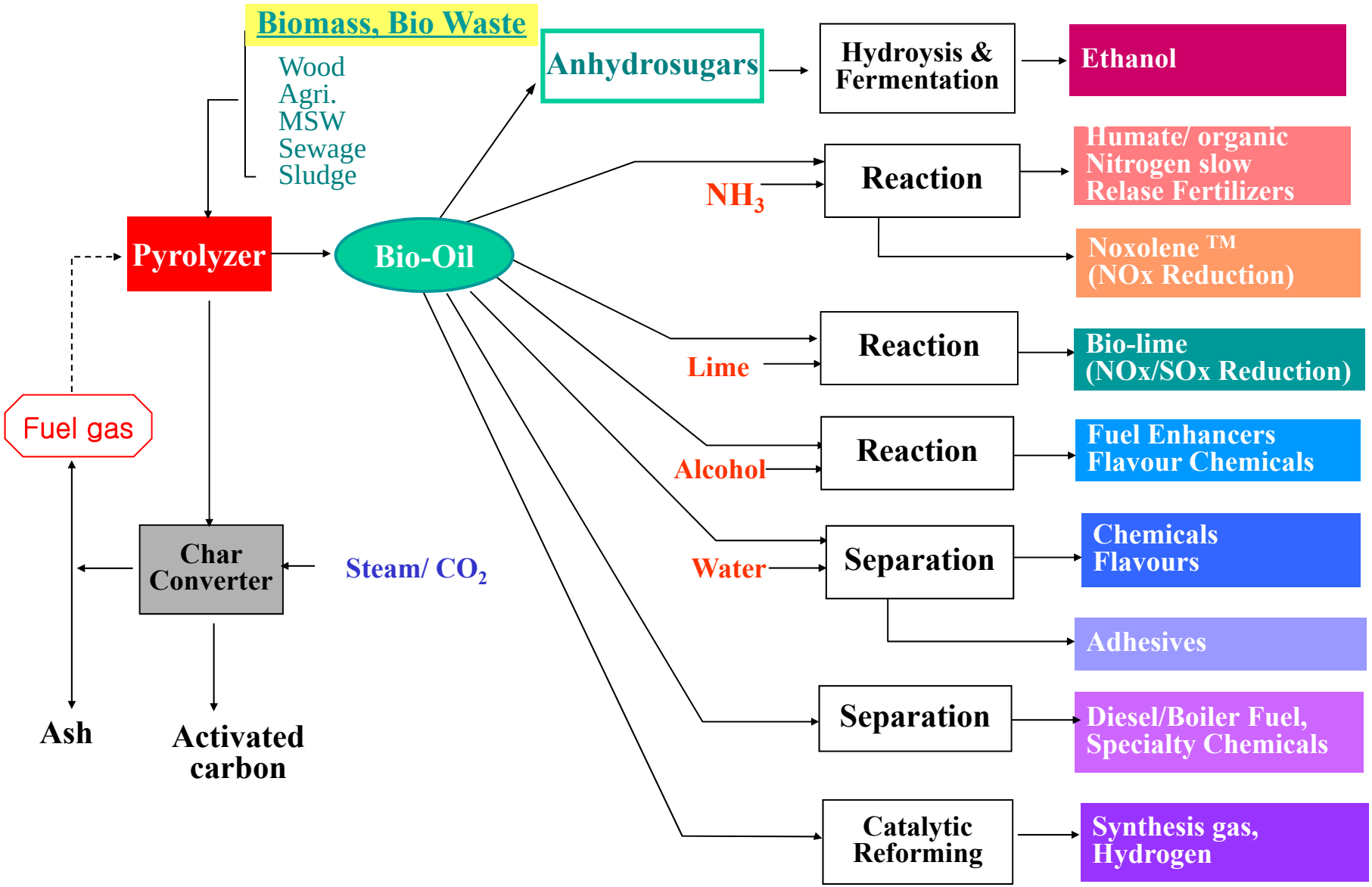
Fertilizer and Soil conditioners

Amino compound와 Bio-oil을 반응
식물에 대해 non-toxic/ 유기성 비료를 천천히 release 함

Acetalizaton and esterification rxn.응용

- 연료로서의 활용
- 물질로서의 활용
  - flavor chemicals
  - octane enhancers
  - solvents, resins, varnishes
  - conversion to ethers

V. Bio-oil의 활용


Biomass, Bio Waste
Wood
Agri.
MSW
Sewage
Sludge
Pyrolyzer
Bio-Oil
Fuel gas
Char Converter
Steam/ CO_2
Ash
Activated carbon
Anhydrosugars
Hydroysis & Fermentation
Ethanol
NH_3
Reaction
Humate/ organic Nitrogen slow Relase Fertilizers
Noxolene ™ (NOx Reduction)
Lime
Reaction
Bio-lime (NOx/SOx Reduction)
Alcohol
Reaction
Fuel Enhancers Flavour Chemicals
Water
Separation
Chemicals Flavours
Adhesives
Separation
Diesel/Boiler Fuel, Specialty Chemicals
Catalytic Reforming
Synthesis gas, Hydrogen