Reaction Mechanism of Coal Liquefaction and Proposed New Process

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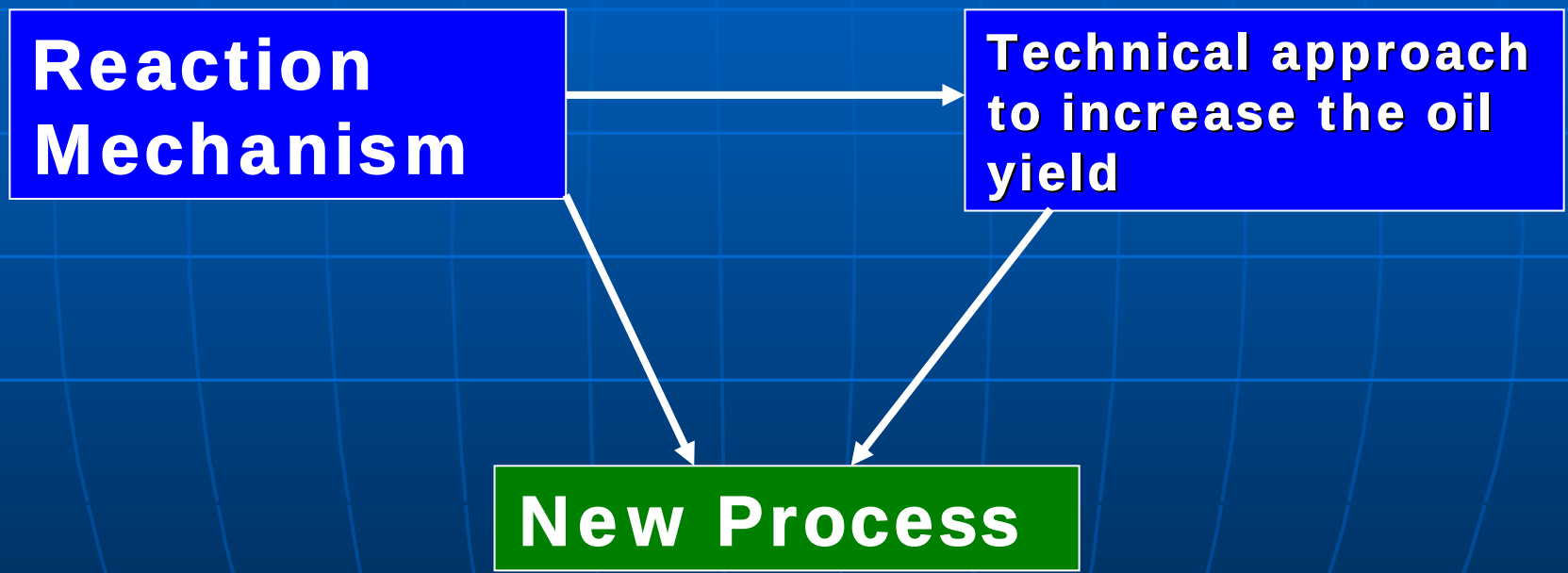
Preface

- Develop coal-base liquefied fuels and advance sequentially demonstration project of coal liquefaction was issued in the eleventh Five Years Program of China Economy and Society Development
- Coal liquefaction: Direct & Indirect

Coal Direct Liquefaction



1. Reaction Mechanism

Coal molecular structure

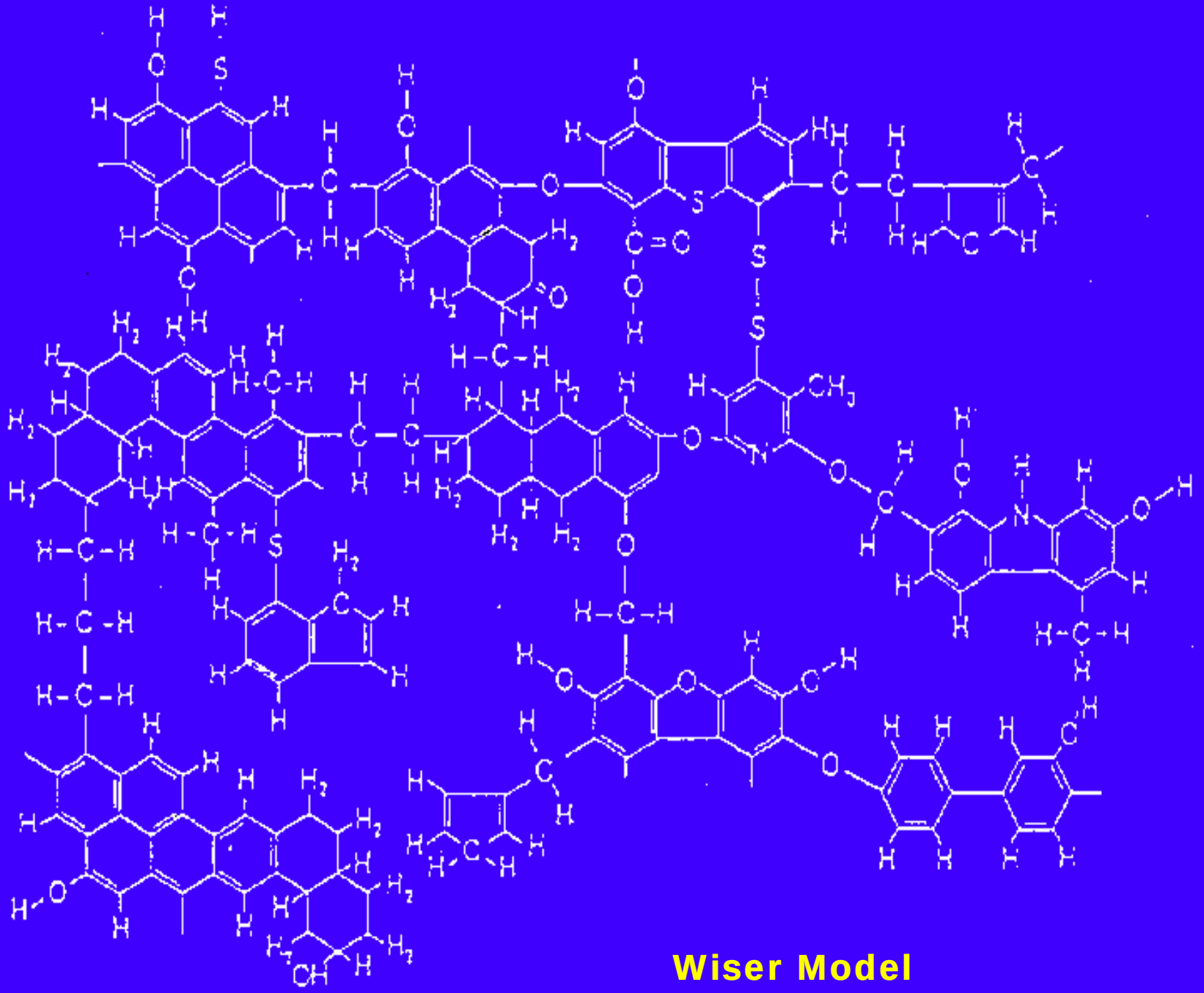
A. Wiser Model

1. Net Structure
2. Poly-aromatic peaces
3. Bridging covalent bonds
4. In the space of the net structures there are some mobile phase components which present smaller molecular size.

Coal Molecular Structure

B. Physically Association Model

- **Wide distribution of molecular size**
- **Associated by ion-bond, hydrogen-bond, π-π electron interaction**
- **Poly-aromatic molecules**



Wiser Model

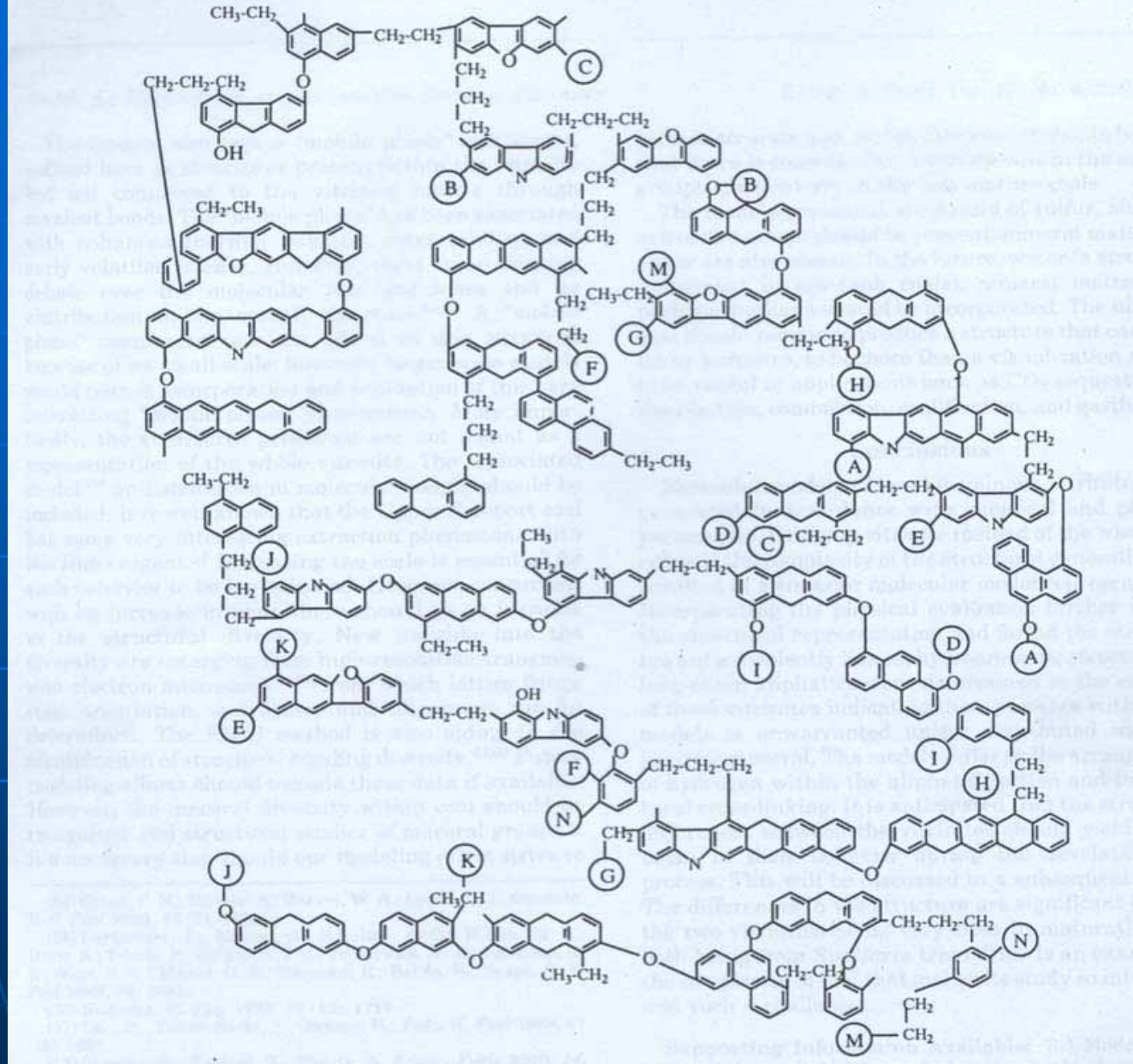
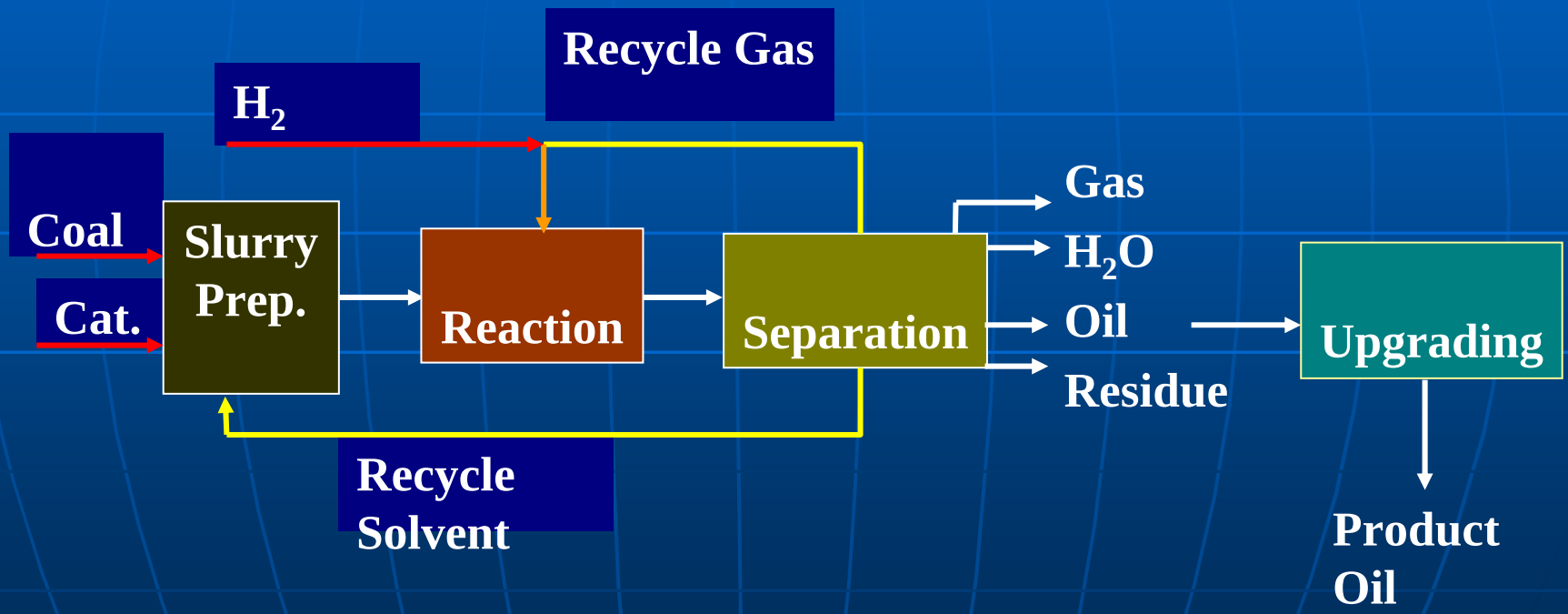


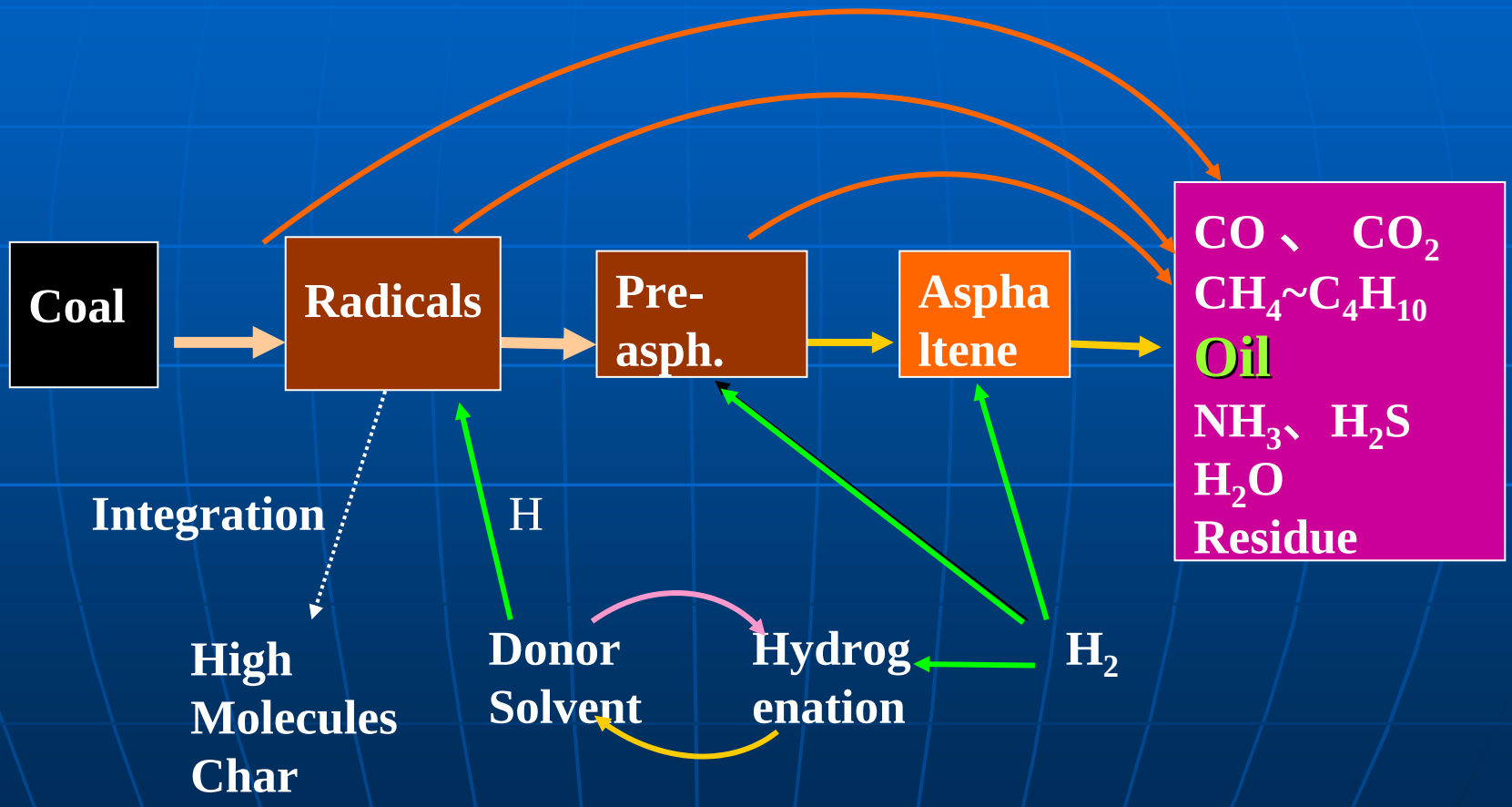
Figure 7. A 2D representation of the LS vitrinite. A connects to A, etc.

Molecular Structure of Lewiston Stockton Coal

Normal Process of Coal Direct Liquefaction



Reaction Mechanism



Radical Chain Reaction of Model Comband

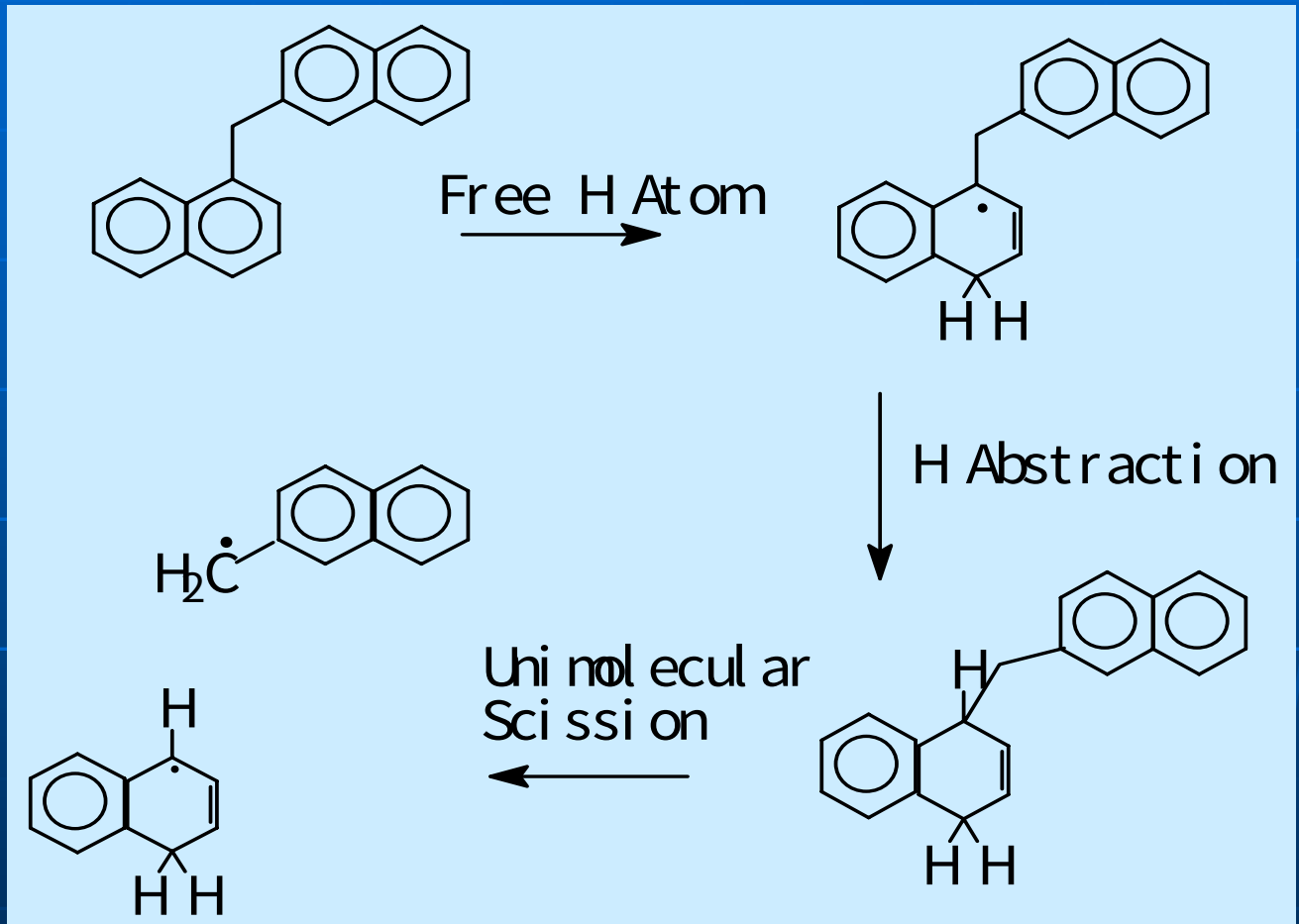
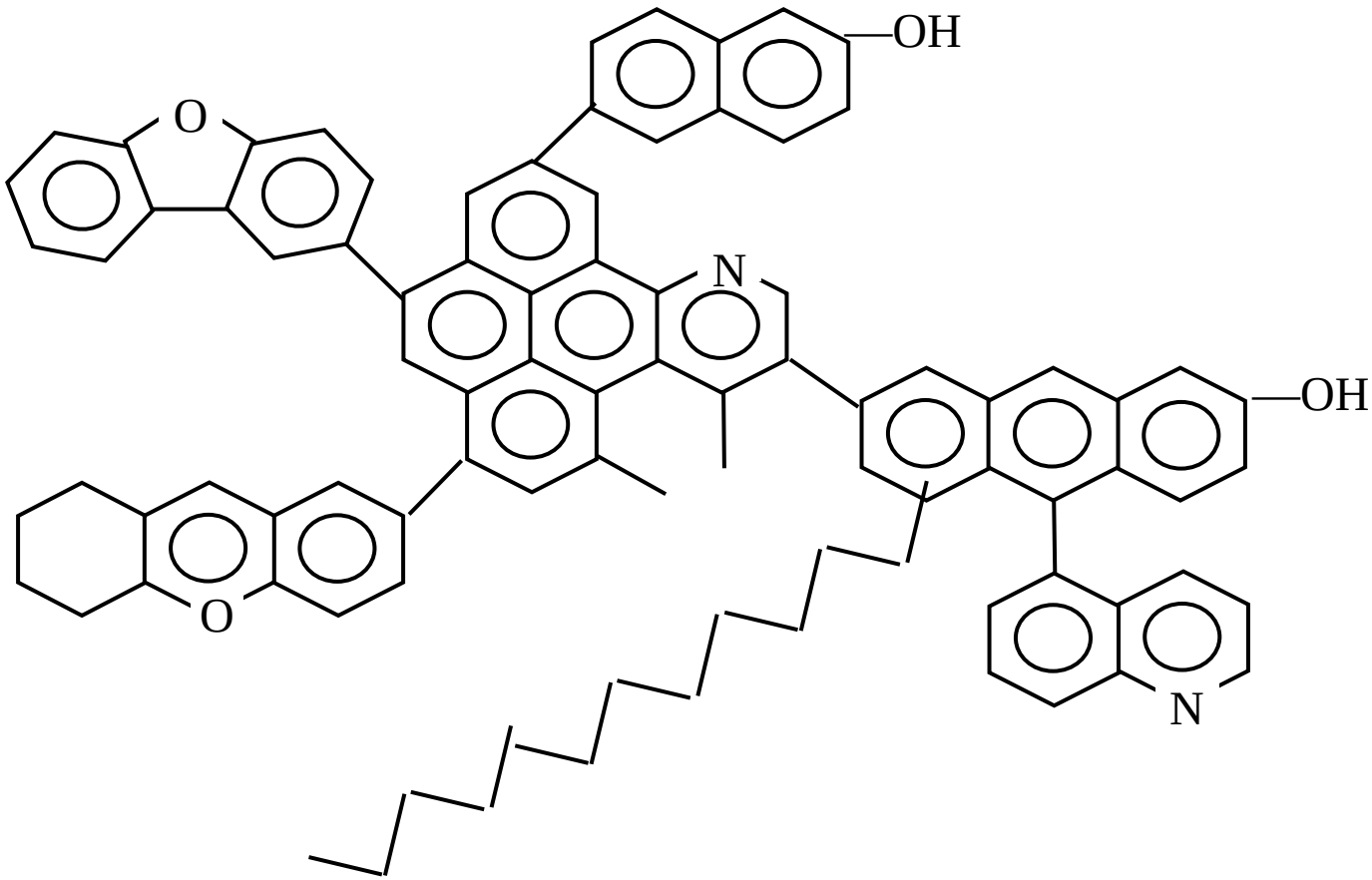
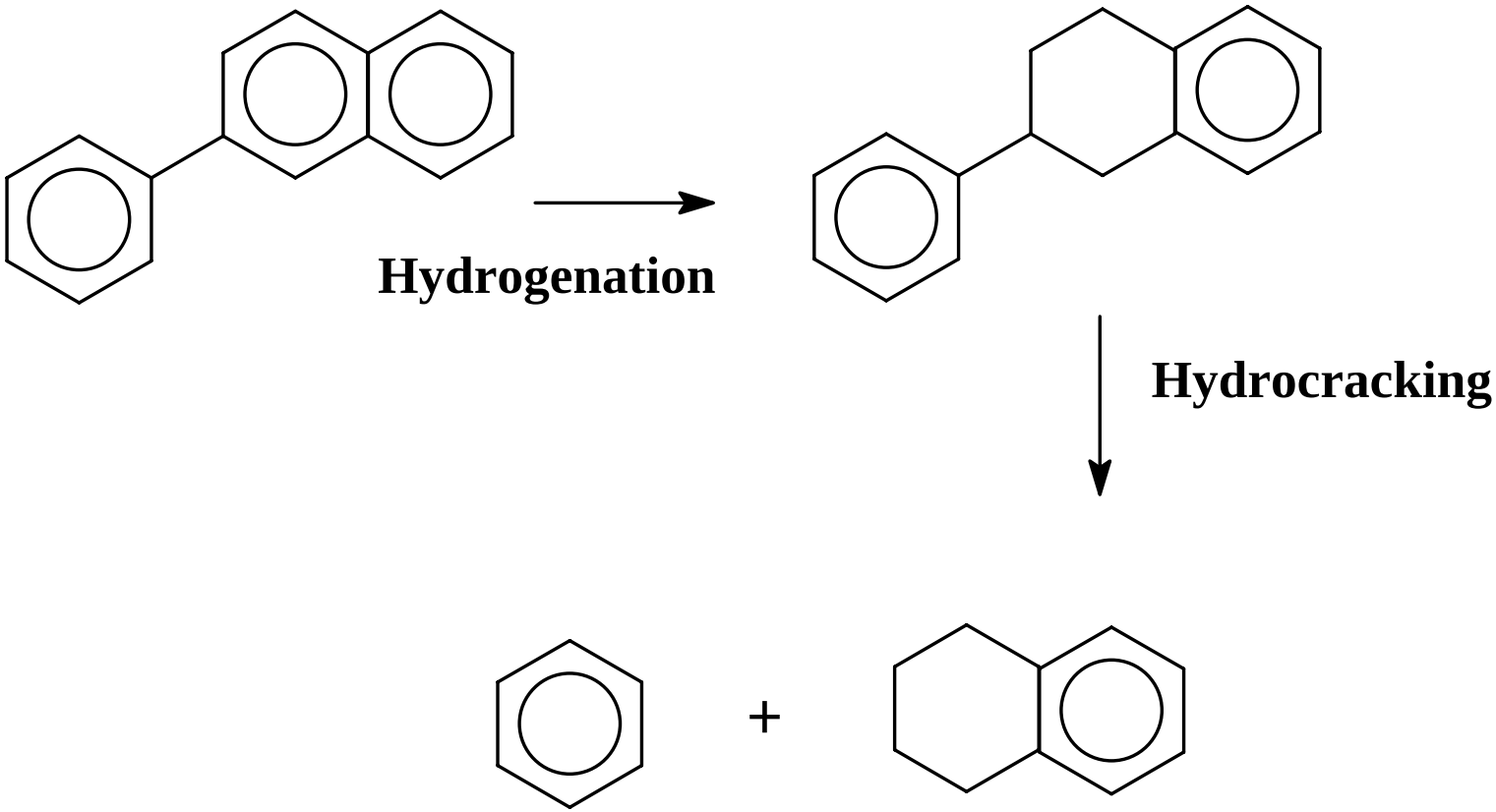


Figure 1. Radical Chain Reaction of Model Compound

Structure of Asphaltene



Hydrocracking of Poly-aromatics



Different reaction rate of coal

Three components with different reaction rate in coal：

M_0 : Reaction rate was very fast, it converted completely with heated just to 450℃

M_0 was equal to 77% for Shenhua Coal

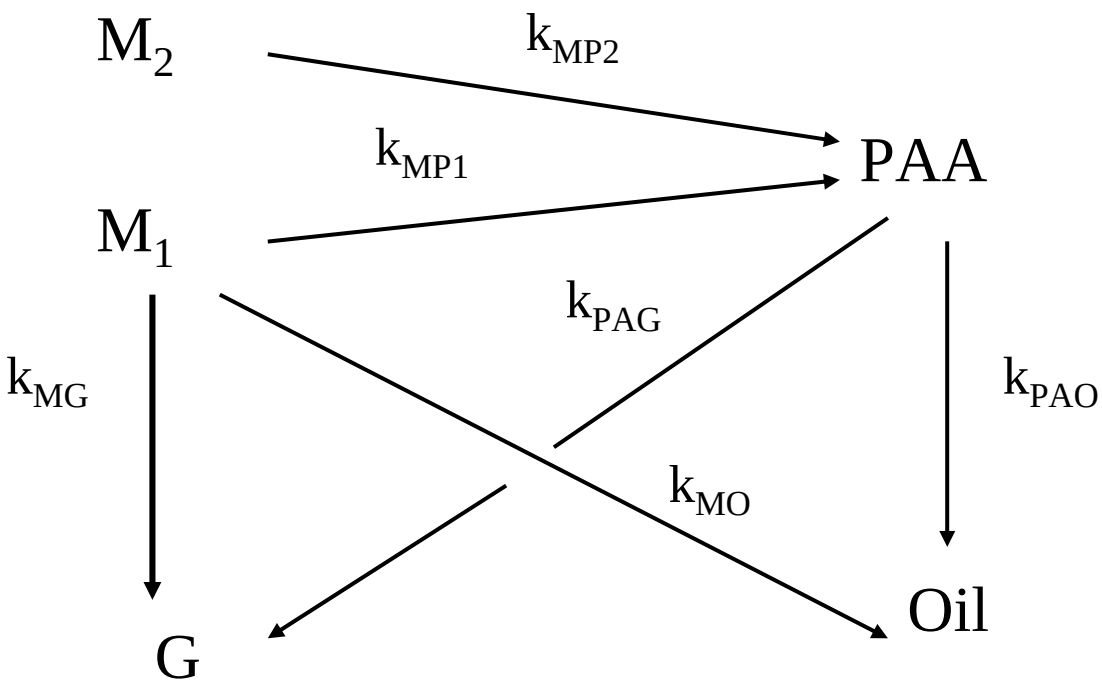
M_1 : Reaction rate was slower than M_0

it was equal to 9.5% for Shenhua Coal

M_2 : Reaction rate was very slow

it was equal to 13.5%

Reaction Net of Coal



Reaction Speed Constants in 2nd Phase

$k_1 = 0.1136\,\mathrm{min}^{-1}$

$k_A = 0.0233\,\mathrm{min}^{-1}$

$k_{MP2} = 0.0059\,\mathrm{min}^{-1}$

- In period of 30min, M1 Reacted Completely, M2 Reacted very Slow
- M2 Reaction offer Conversion increased 3.92%
- Asphaltene conversion is the rate limit reaction in the second phase

Brief Summary

- **Two phase undergone with coal liquefaction**
- **First phase is coal pyrolysis to produce radicals**

The reaction is very fast

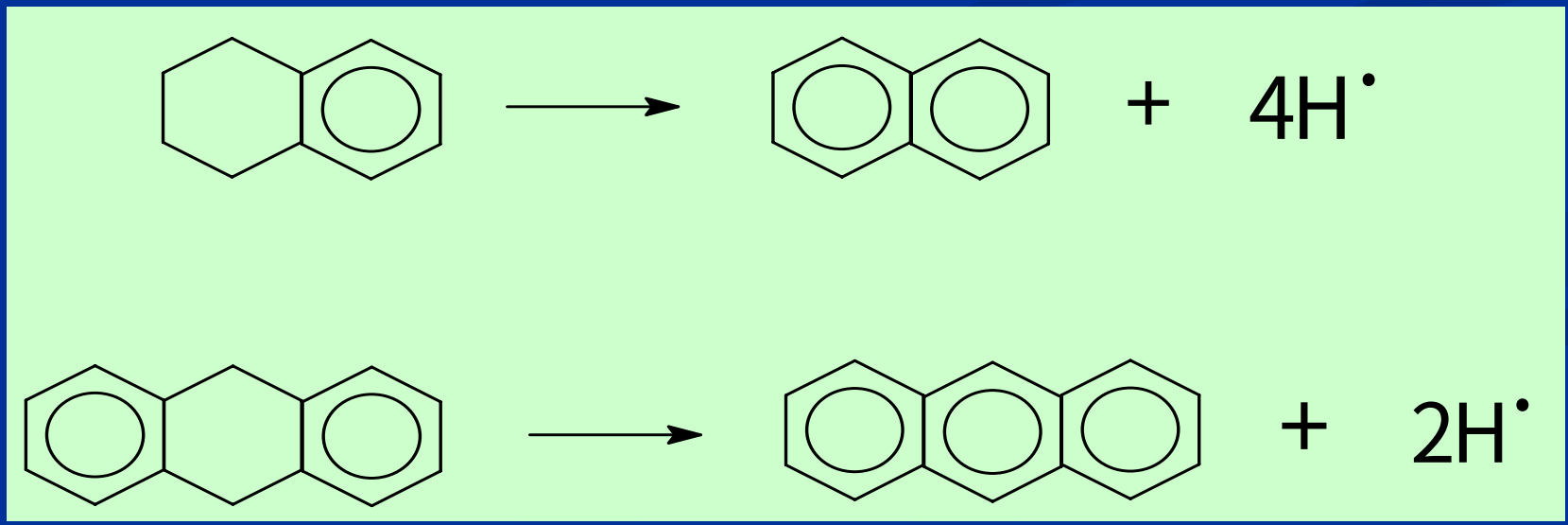
- **Second phase is asphaltene hydrogenation and hydrocracking.**

The reactions are slower

2. Technical approach to increase the oil yield

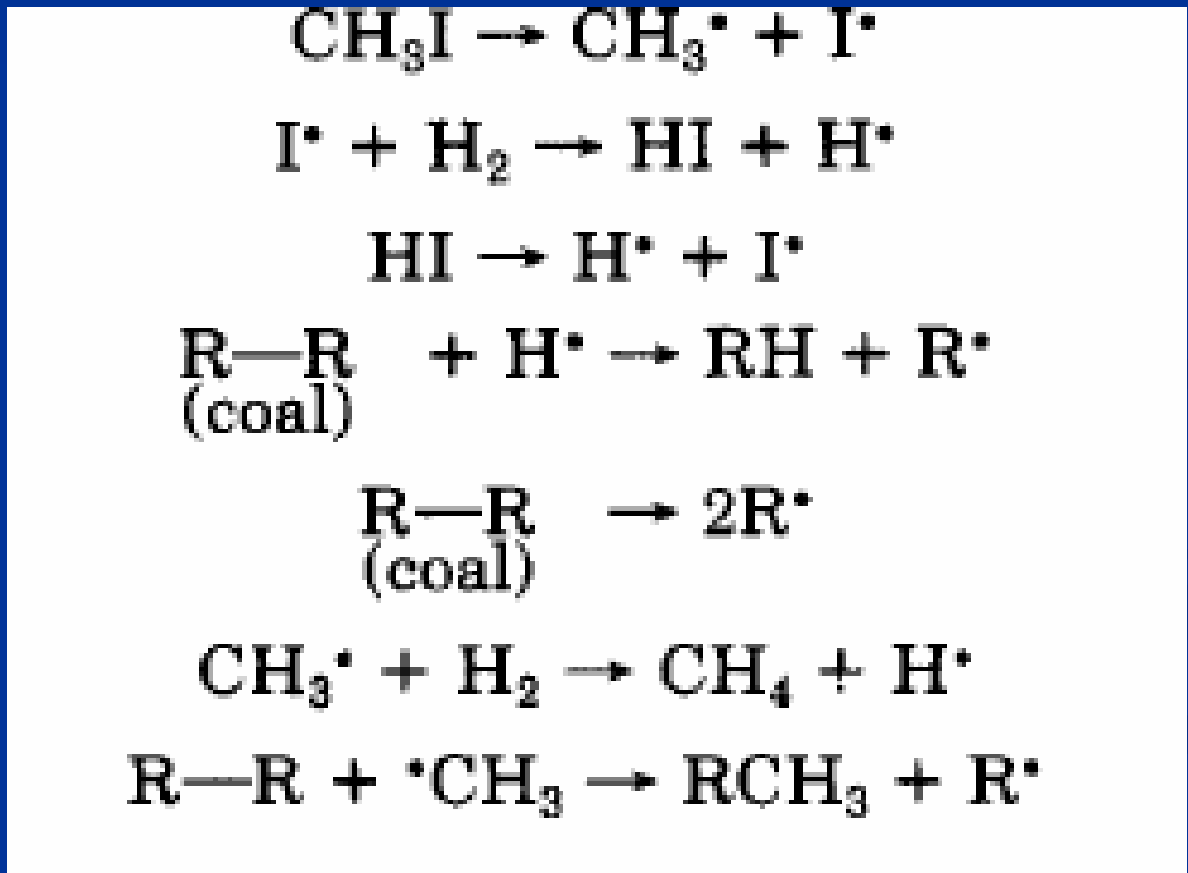
- 2.1 Increase hydrogen donor ability of the solvent

Saturated partly poly-aromatics



- **2.2 Addition of some substance producing easily a lot of small radicals**

  Such as Iodomethane , Lignin , Lignite



- **2.3 Decrease the speed rate of production of radicals from coal**

Temperature Program

Settle a period under low temperature

350℃ —— 400℃ —— 430℃

380℃、15min —— 450℃、45min

- **2.4 Enhance the reaction severity in the 2nd phase**

Enhance Temperature, Have a Optimum Temperature

Enhance H_2 Pressure: Total Pressure, H_2 Content

Extend Reaction Time:

Increase the Volume of Reactor

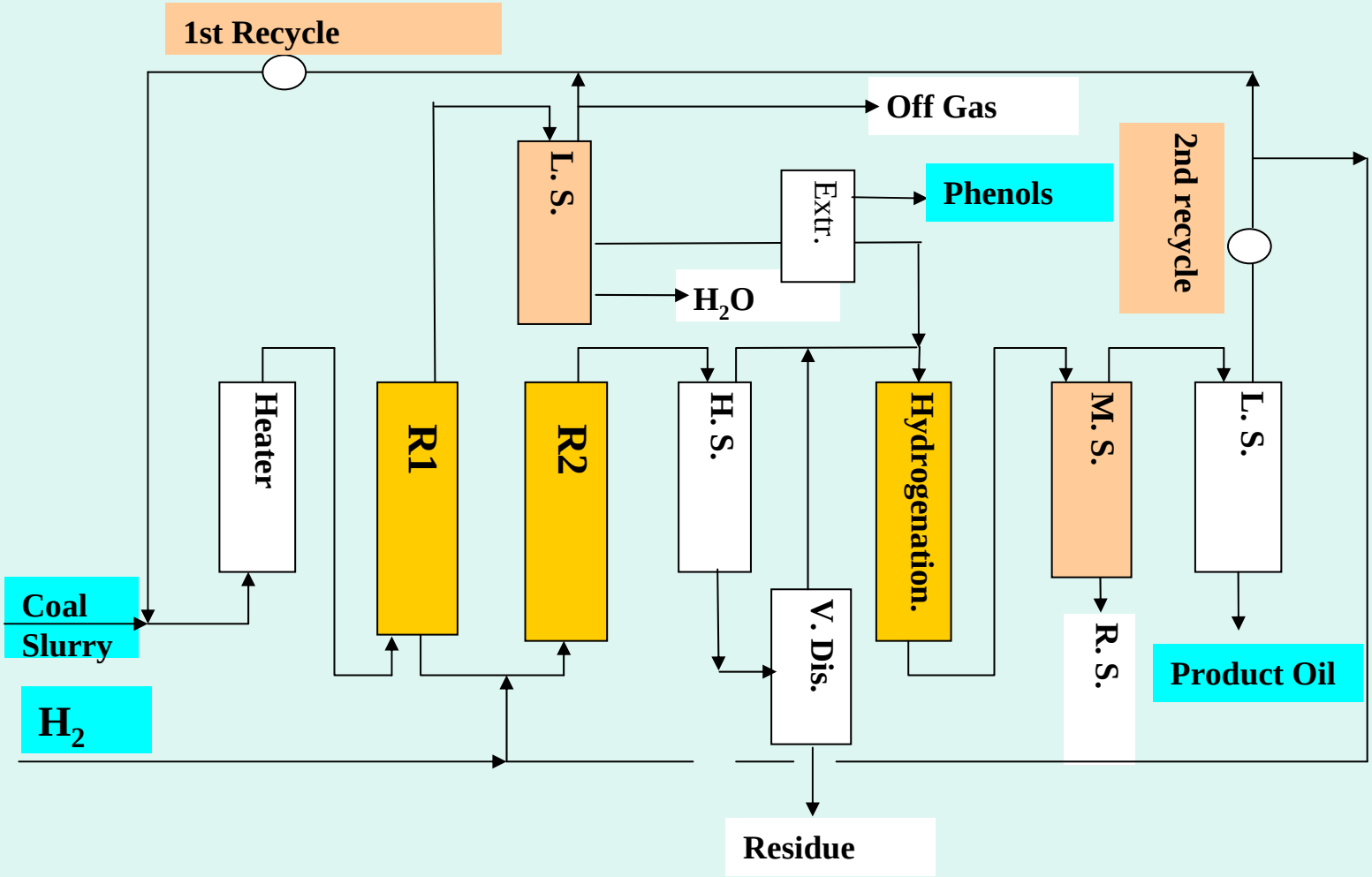
Decrease Gas Hold-up

- **2.5 Improve hydrogenation activity of the catalyst**

Addition of Second Active Component

Soluble Mo, Ni

3. Design Ideas of New Process



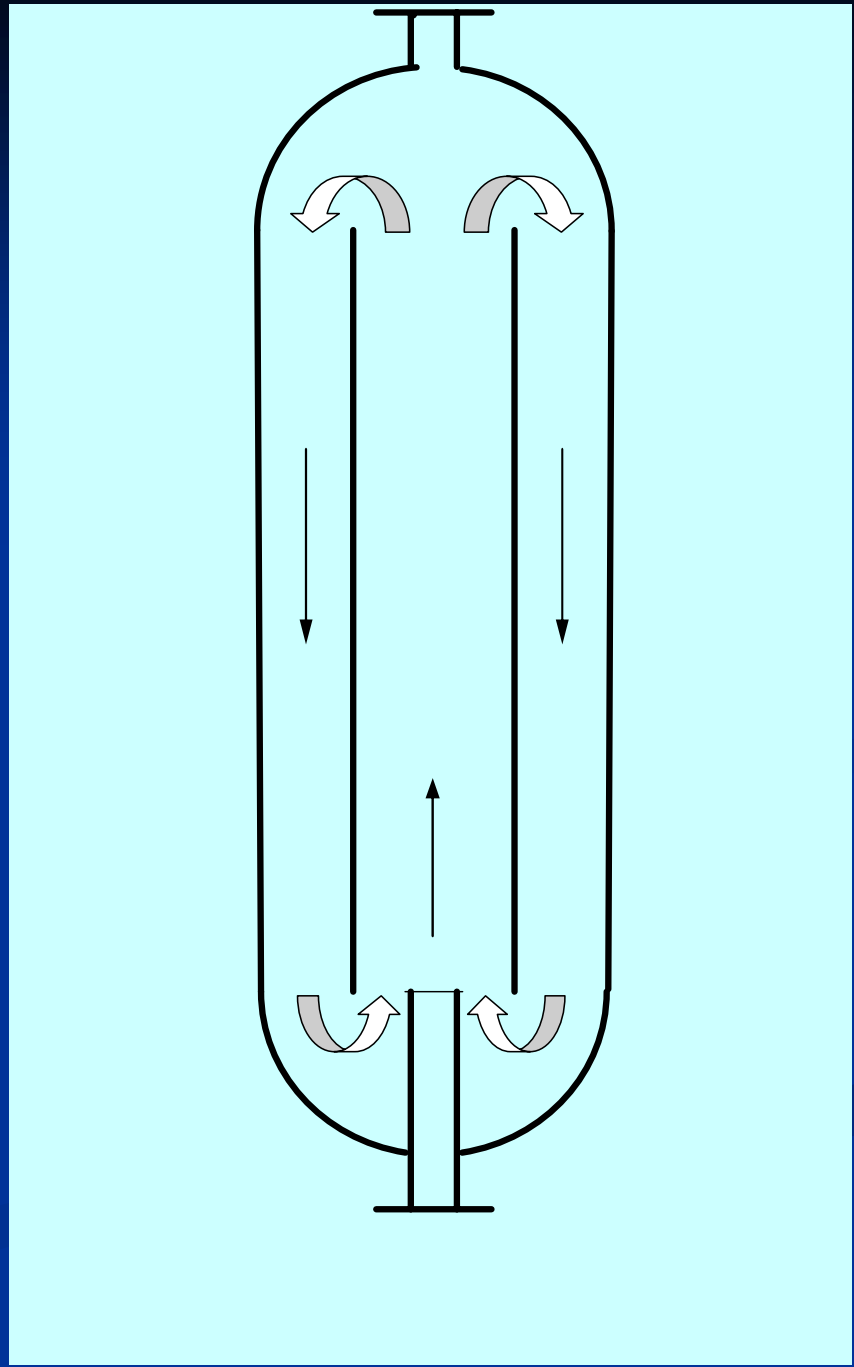
CDCL Process Highlight

3. Design Ideas of New Process

- **Two Stages Reaction**
- **Addition of Radical Source Substance**
- **The First Reactor Is also Separator**
- **Inner Recycle Gas-lift Reactor**
- **On-line Fixed Bed Hydrogenation Reactor**
- **Make-up H_2 Entry to 2nd Reactor, Two hydrogen recycle systems**
- **Phenols Extraction of Light oil**
- **Medium Temperature Separator for Solvent Separation**

Gas-lift Reactor

- Homocentric Flow Guide Tube
- Gas Expanding Used as Impetus
- Slurry Recycle Motion in Reactor



Advantages of the gas-lift reactor

- Slurry recycle pump would be leaved out
- Back mixing mode
- Decreasing the gas hold-up
- Preventing the solids sedimentation

4. Results of Primary validate experiments

- **Autoclave**
- **Shenhua Coal**
- **H_2 primary pressure：8.4 MPa**
- **First Stage：400℃，15min**

  Second Stage：450℃，45min

  Contrast experiment：450℃，60min

4. Results of Primary validate experiments

Coal/Solvent=45/55、863 Catalyst

℃/ min	H2 Cons.	Conv.	Gas	COx	C_1-C_4	Preas.	Asph.	Oil	H_2O
400/ 15	1.56	67.93	5.06	3.01	1.61	17.60	15.46		
450/ 45	2.62	91.24	9.27	1.15	8.10				
Total	4.18	91.24	14.32	4.16	9.70	1.74	8.44	58.94	11.97
450/ 60	4.55	87.96	14.16	3.63	10.23	0.00	7.42	58.47	12.47

5. Conclusion

- Fast & slow reactions of two phases Mechanism
- Two stage reaction process
- Results of primary experiments validated some design ideas of new process
- The technical development and feasibility study of the new process have to be much done in the future

Thank You