



Extension of gas phase models to liquid phase reactions

hydrodenitrogenation of pyridine

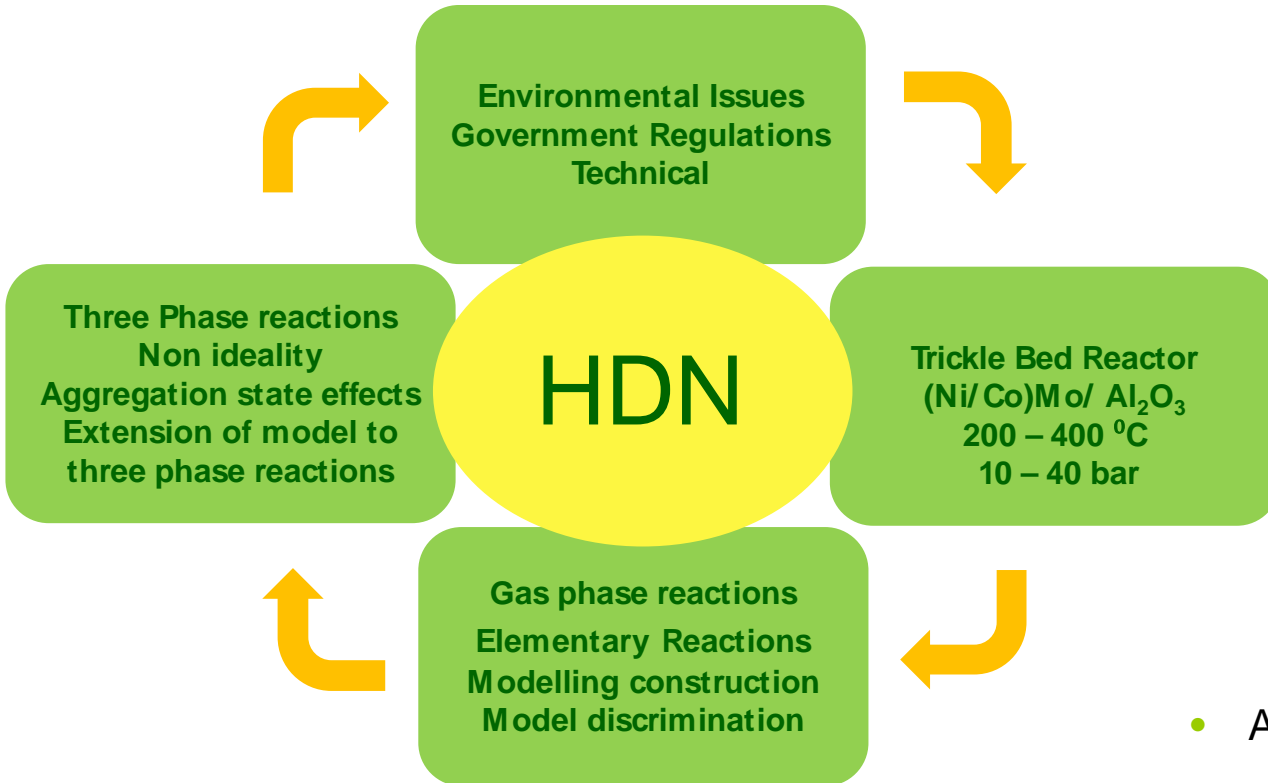
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28th February, Hull UK

Curriculum Vitae



- **Bachelors in Chemical engineering** (2003-2007)
 - RV College of Engineering, Bangalore – India
 - Development and testing of organic dyes
- **Masters in Chemical engineering** (2007-2010)
 - TU Dortmund, Dortmund – Germany
 - Catalytic transfer hydrogenation of Thiophene
 - Fraunhofer UMSICHT, Oberhausen – Germany
- **Doctoral Research** (2010 - present)
 - Ghent University, Ghent – Belgium & BP plc, Sunbury - UK
 - Kinetic studies on Hydrodenitrogenation of pyridine

Introduction



- Answering basic questions
 - Why ?
 - How ?
 - What ?

Contents



- Research motivation & methodology
- Thermodynamic non-ideality in the liquid phase
- Comparison : Gas and liquid experiments
- Liquid phase experimental program
- Gas phase modelling and extension to liquid phase
- Results and conclusions
- Appendices

Research motivation



- Research aim
 - Elementary reactions, to understand the underlying reaction mechanisms
 - Comparison of gas and three phase reactions
 - Scale up to pilot/industrial scale data
- Some previous work
 - Case study by Bera et.al, on Naphthalene hydrogenation
 - Published work on Tetralin hydrogenation by Guevara et.al
 - Not a significant amount of work done with respect to HDN

Extended set of gas phase experimentation

- Operating conditions
- Reaction pathway
- Detailed kinetics
- Model construction and discrimination
- Evaluation estimated parameters

Limited three phase experimentation

- 3-phase conditions on
- Formation of new compounds
- Solvent adsorption
- Assessment of liquid phase non ideality

Industrial reactor simulation

- Validation of data available from industrial / Pilot plant studies

Thermodynamic non-ideality in the liquid phase



- Non ideality in mixtures



- Chemical potential : Independent of standard state used

$$\mu_i = \mu_{i \text{ standard}} + RT \ln a_i$$

- Condition for phase equilibrium

$$\mu_i^v = \mu_i^l \quad i = 1, \dots, n$$

$$f_i^v = f_i^l \quad i = 1, \dots, n$$

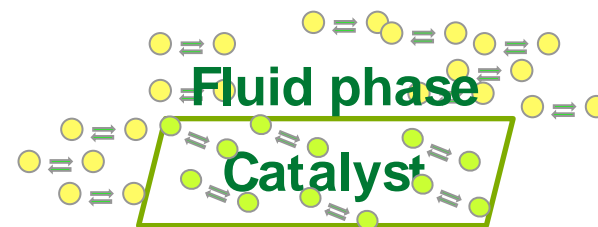
- Basis of V-L relationships : Relate fugacity to compositions and intensive properties (T, P)

$$f = f^n(T, P, y_i)$$

Thermodynamic non-ideality in the liquid phase



- Effect of aggregation state
 - Chemisorbed and non chemisorbed species
 - Description of kinetics, independent of aggregation state
 - Difference between vapour and liquid phase kinetics is situated in the chemisorption step



- Methods and correlations (φ_i)

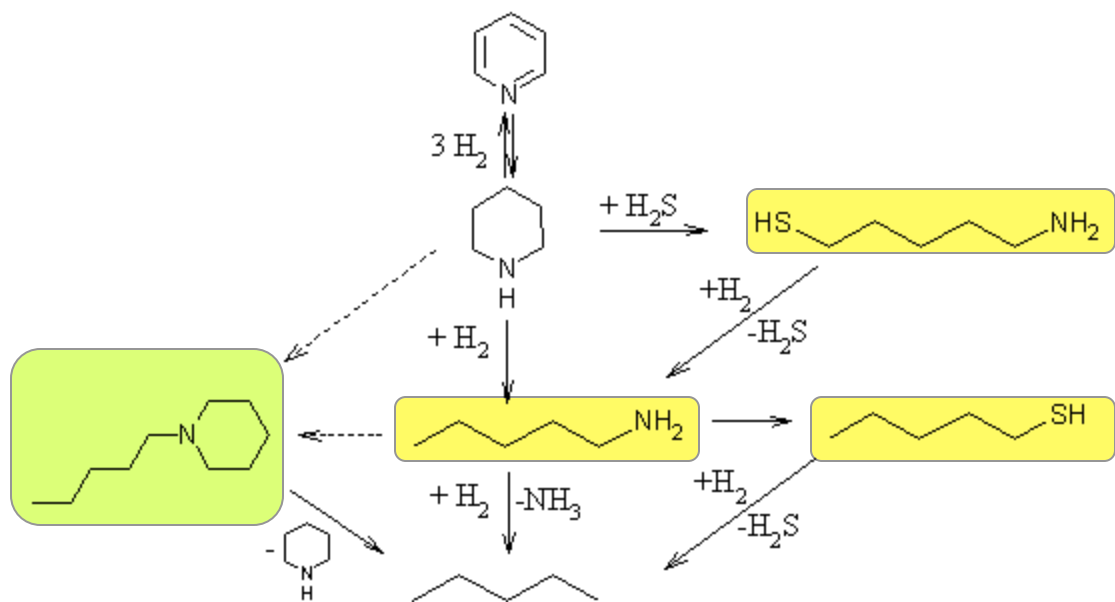
$$f_i = \varphi_i \cdot P y_i = \varphi_k C_i V_m P \quad \varphi_i = \frac{f_{i,G}}{P y_i}$$

Comparison : Gas and three experiments



Program	Gas Phase	Three Phase
Reactor type	Berty type (CSTR)	Robinson Mahoney (CSTR)
Temperature range (K)	573 – 633	543 – 613
Pressure (MPa)	1.5 – 4.0	6.0 – 8.0
H ₂ /pyridine (mol/mol)	80 – 600	10 – 15
Space time (kgcat s/mmol)	0.36 – 1.8	0.65 – 3
Solvent/pyridine	40	20 - 40

Introducing the compounds



- Species not observed
- Observed in liquid phase experiments only

- Pentylpiperidine observed in the liquid phase experiments only
 - observed with 2D GC - MS analysis
 - due to the varying operating conditions
 - higher bi molecular reactions in the liquid phase
- Highly reactive/unstable intermediates not observed during analysis

Three phase experiments

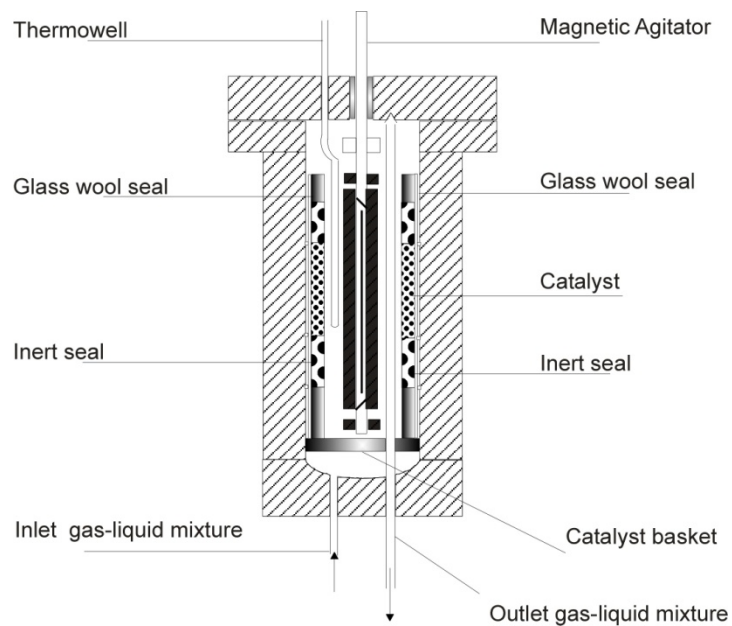
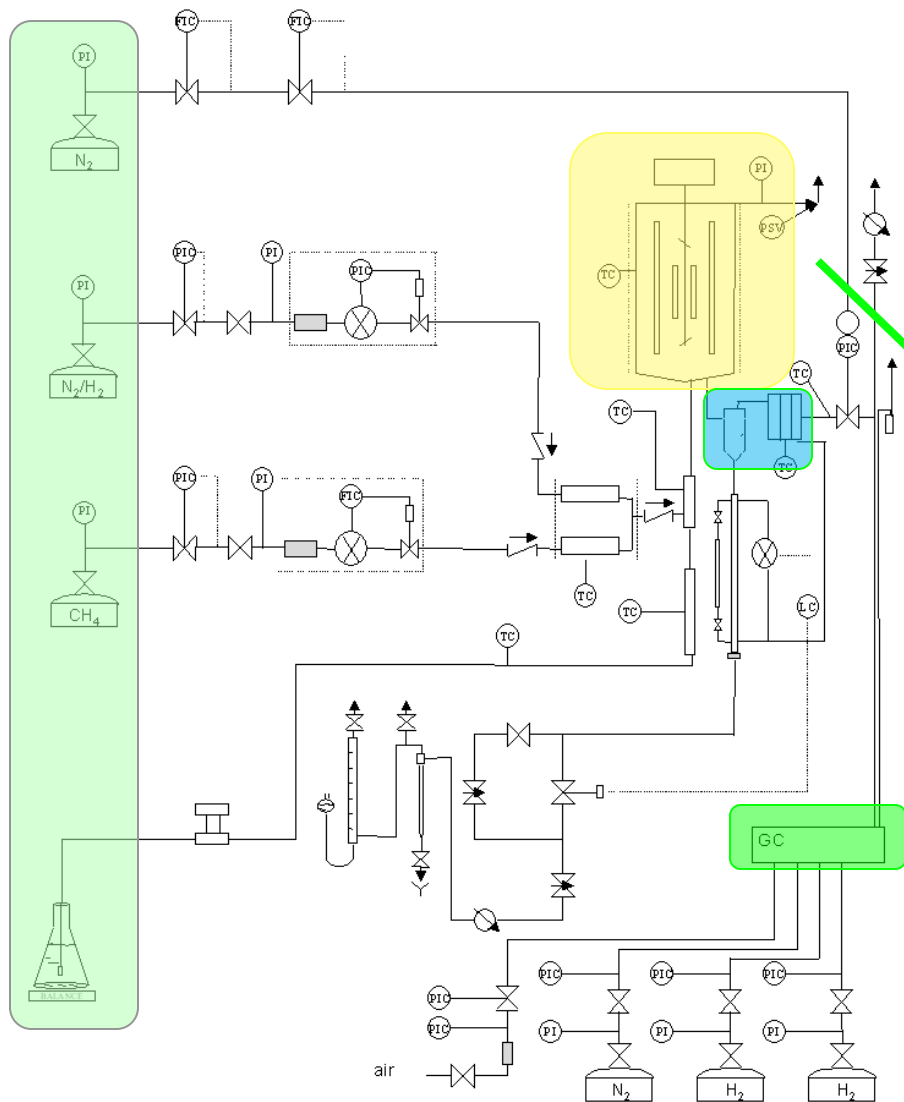


- Aim
 - Study effects of various process parameters on reaction kinetics
 - Difference in the kinetics of the reactions due to change in aggregation state
 - Acquisition of intrinsic kinetic data
- Preliminary Preparations
 - VLE calculations for phase equilibrium analysis
 - Thermodynamic equilibrium analysis
 - Verification of kinetic regime (Eurokin spread sheet)
 - Carberry number : MT limitations : G–L, L–S, G–S
 - Weisz Modulus : Intraparticle diffusion : Pyridine, H₂
 - Mears criteria : Temperature gradient : L–S

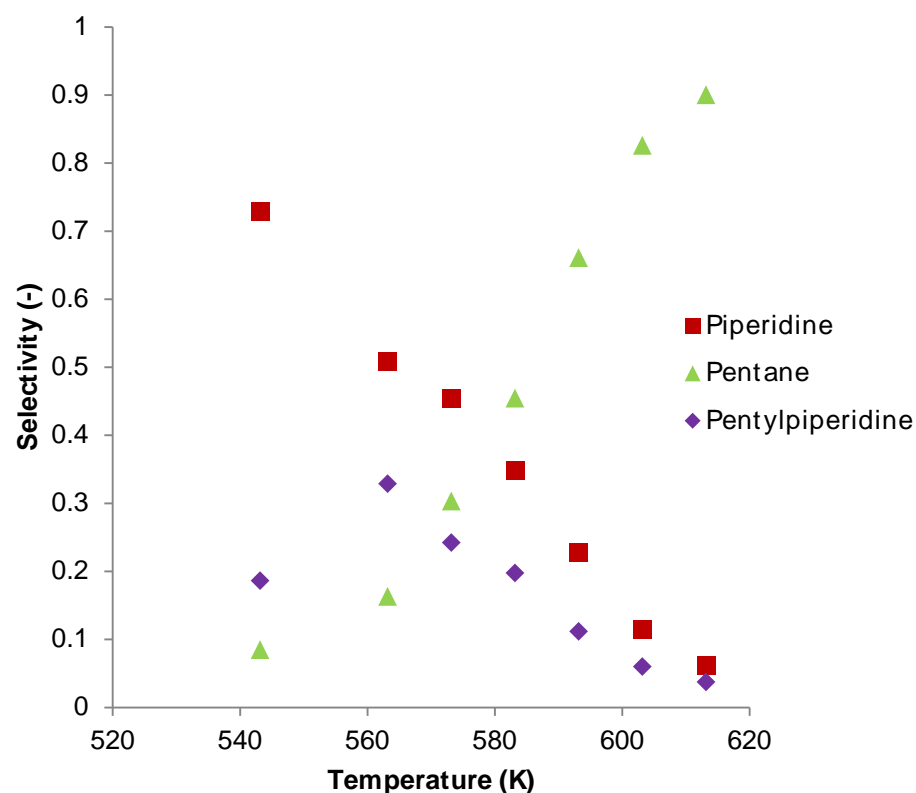
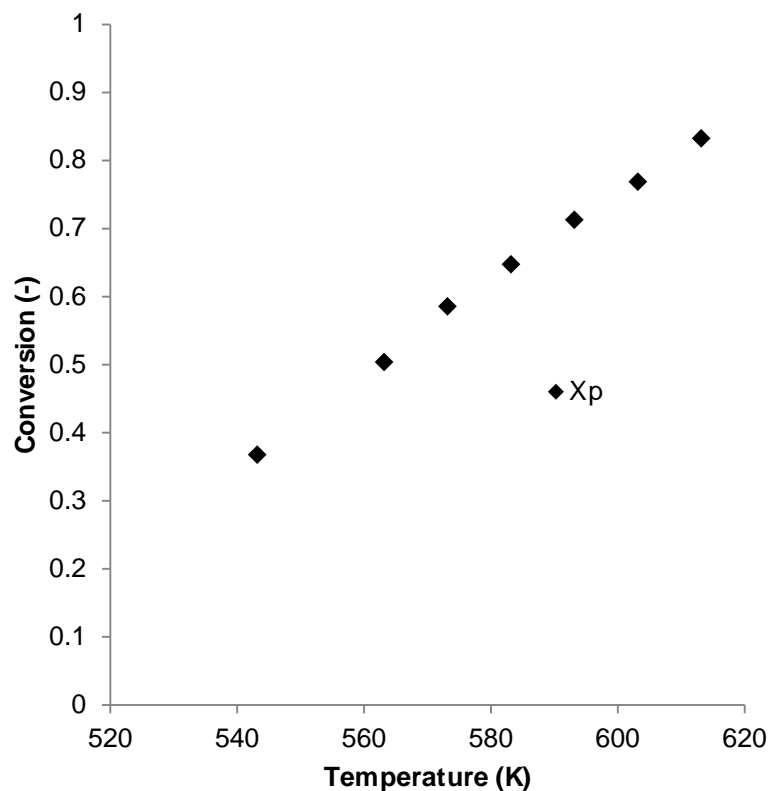
Experimental setup & reactor



Experimental setup showing different sections

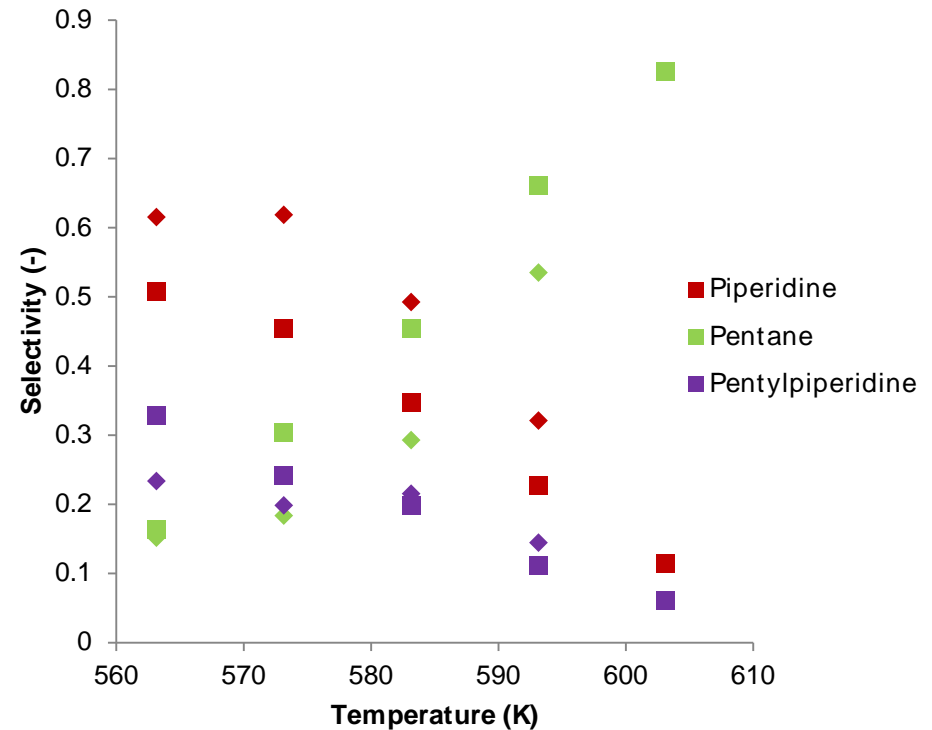
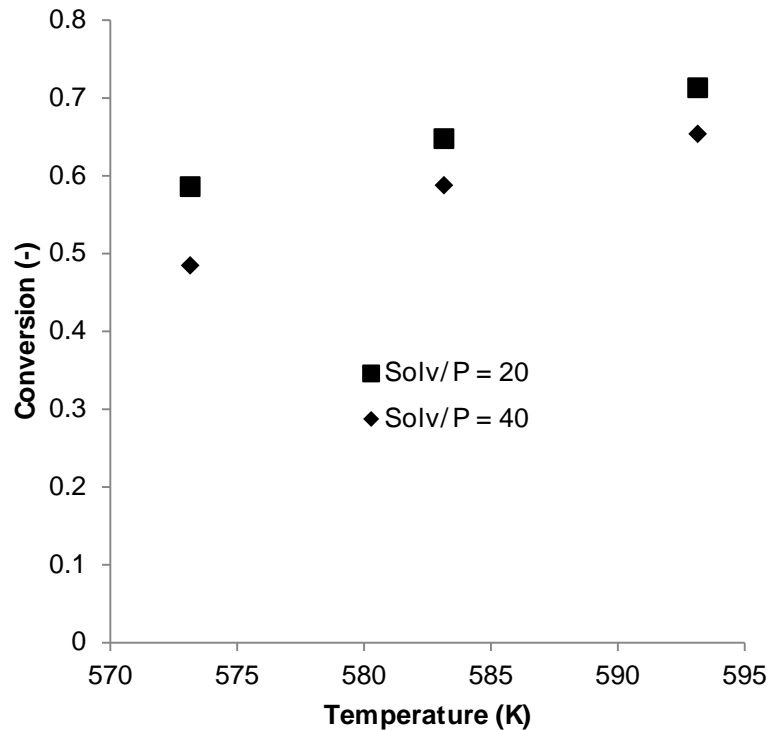


Experimental results (1)



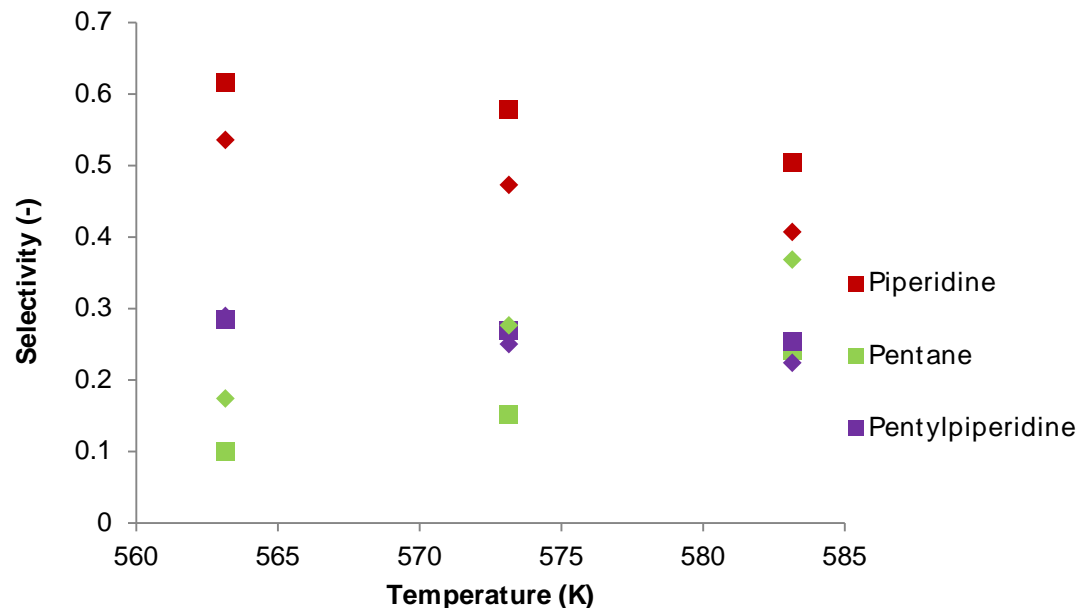
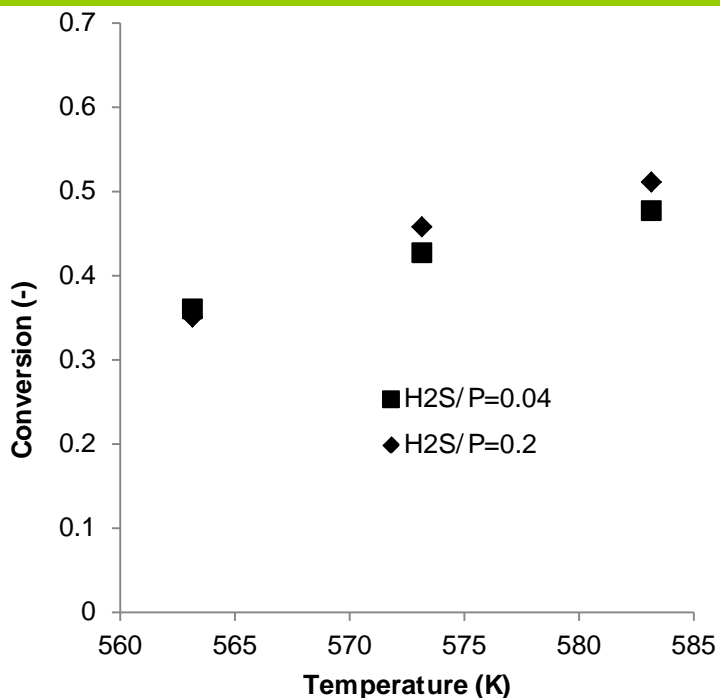
- Increased selectivity towards pentane implies higher C – N bond scission
- C-N bond breaking is temperature dependant
- Pentyl piperidine selectivity decreases meaning disproportion is less likely

Experimental results (2)



- Positive reaction order with respect to Pyridine
- Competitively adsorbing solvent

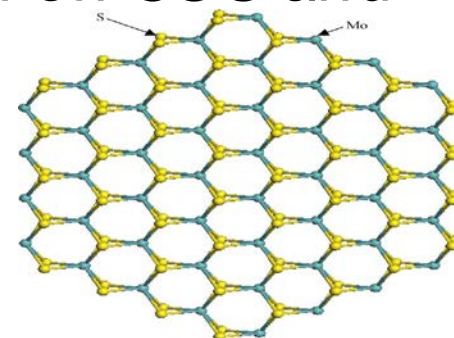
Experimental results (3)



- H₂S has positive effect on the C-N bond scission :
 - Higher hydrocarbon yield at higher H₂S/P
 - Lower intermediate piperidine yield
- Substitution pathway is more pronounced at higher H₂S flow rates

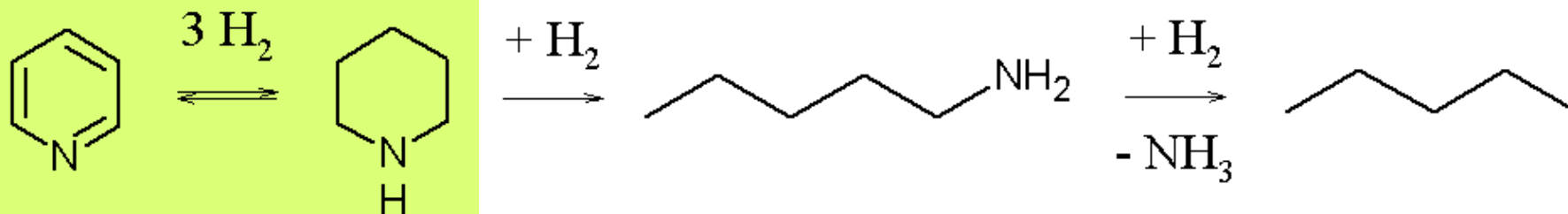
Model assumptions¹ :

- **Sulphided NiMo catalyst**, 2 active sites at the edges :
 - Coordinatively Unsaturated Sites (CUS, ‘ * ’)
 - Sulphur anion sites (SA, ‘ S²⁻ ’)
- Dissociative adsorption of H₂ and H₂S, both on CUS and SA
 - Heterolytically, *Ex. : H₂ + * + S²⁻ → H* + S²⁻H⁺*
 - Homolytically, *Ex. : H₂ + 2 * → 2 H**
- Adsorption of hydrocarbon and nitrogen species on CUS

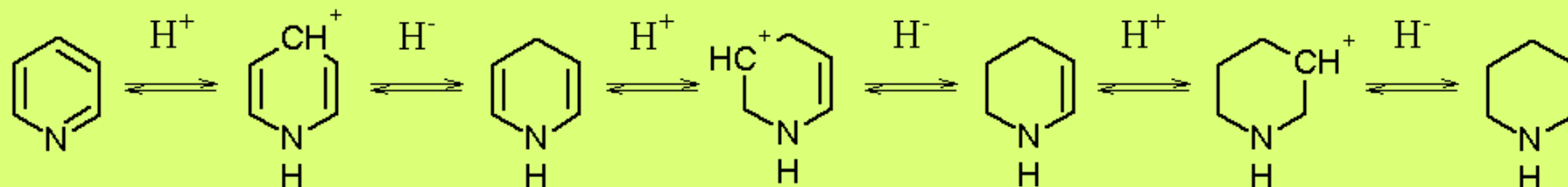


¹Romero, C.M.C., J.W.Thybaut, and G.B. Marin,

Reaction mechanism : Gas phase modelling

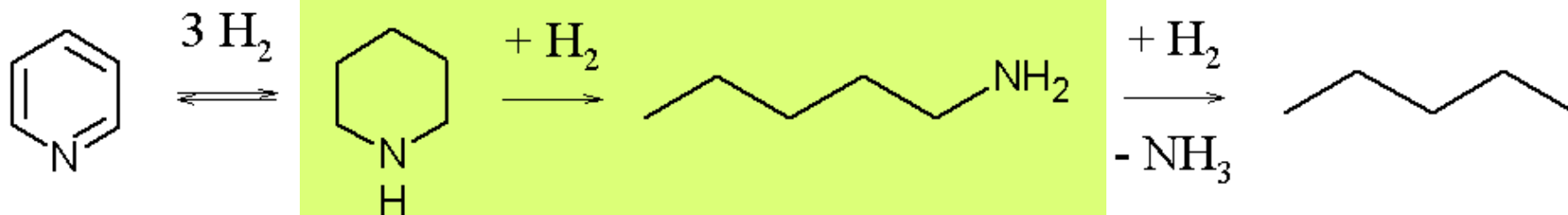


Hydrogenation

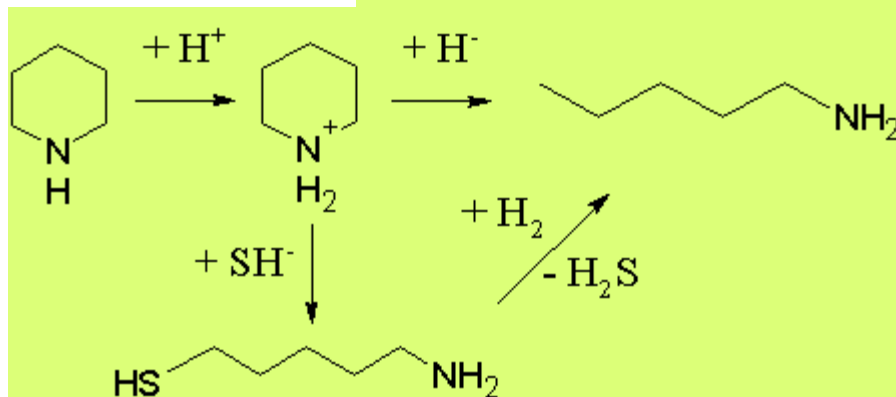


- Hydrogenation occurs through successive H additions
 - Homolytic adsorption H_2 , hydrogen additions from CUS or SA
 - Heterolytic adsorption H_2 , proton or hydride addition first
 - Each hydrogen addition is potentially RDS

Reaction mechanism : Gas phase modelling

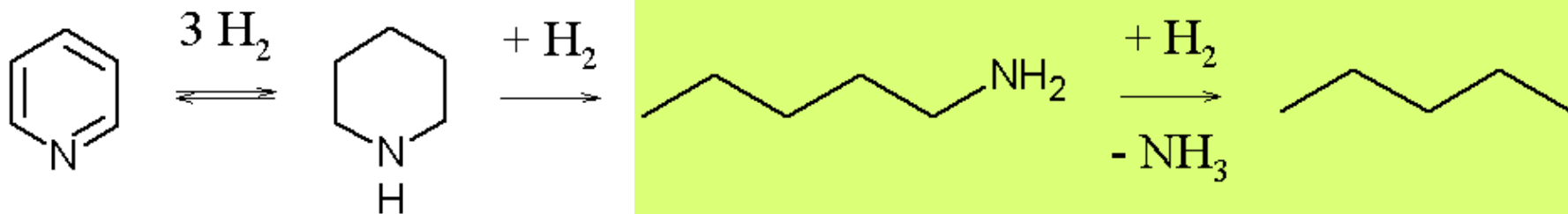


C-N bond scission of piperidine

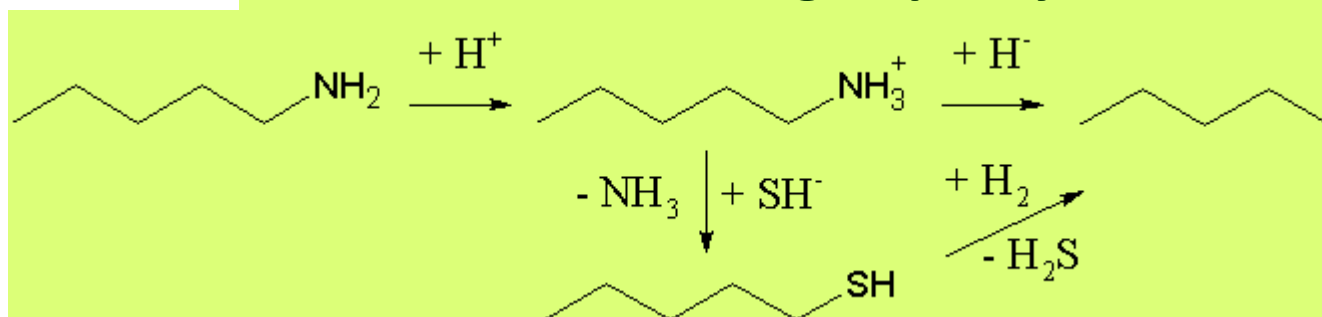


- Multi-step network :
 - Protonation piperidine
 - Substitution via SH addition
 - Thiol intermediate
 - SH-group is good leaving group
- **2 potential RDS**
(protonation or ring opening)

Reaction mechanism : Gas phase modelling



C-N bond breaking of pentylamine



- Analogous as piperidine hydrogenolysis
- Hydrogenolysis of pentylamine occurs instantaneously

Summary : Gas phase modelling



- Development of gas phase model
 - Based on experiments in gas phase
 - Model discrimination performed between 48 rivals
 - Based on physical and statistical significance, Model corresponding to RDS : 3rd Hydrogen addition and 2nd hydrogenolysis step

$$R_{P \rightarrow PP} = k_{p,+} K_{P-PH_2} K_{H_2} K_P C_*^2 \sqrt{\delta} \mu \left(P_{H_2} P_{C_5H_5N} - \frac{1}{K_{Equi}} \frac{P_{C_5H_{10}NH}}{P_{H_2}^2} \right)$$

$$R_{PP \rightarrow PA} = k_{PP} K_{PP-PPH} K_{PP} \mu P_{C_5H_{10}NH} C_*^2$$

$$\delta = 1 + K_P P_{C_5H_5N} + K_{PP} P_{C_5H_{10}NH} + K_{NH_3} P_{NH_3}$$

$$\mu = K_{H_2} P_{H_2} + K_{H_2S} P_{H_2S}$$

Extension to liquid phase reactions



- Taking into consideration the non ideality

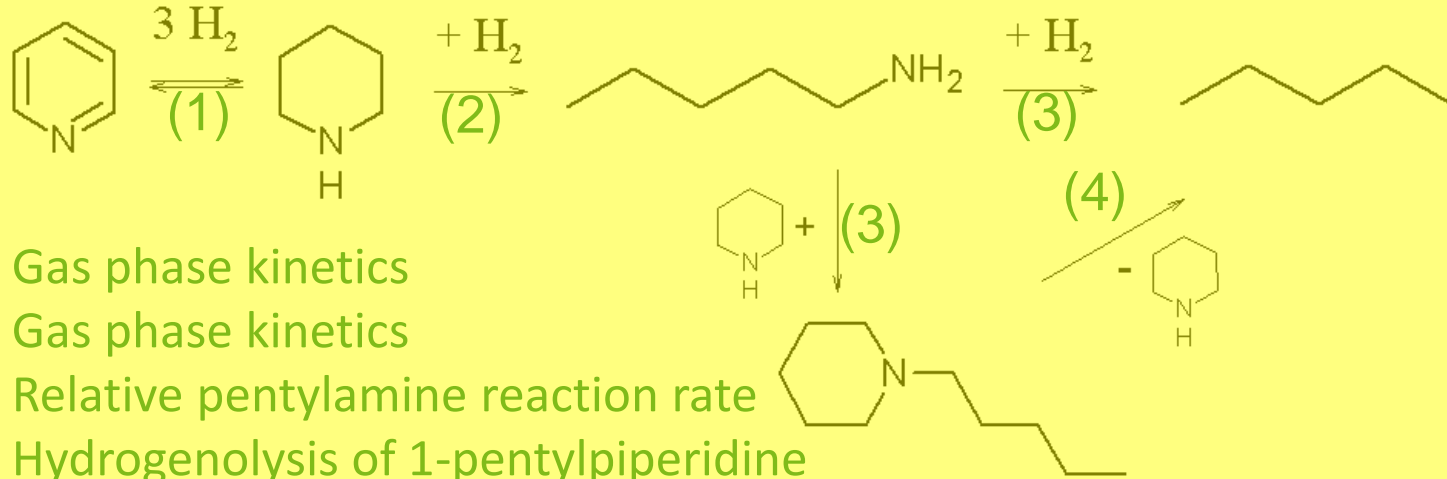
$$\left\{ \begin{array}{l} r_{P \rightarrow PP} = k_{p,+} K_{P-PH_2} K_{H_2} K_P C_*^2 \sqrt{\delta} \mu \left(f_{H_2} f_{C_5H_5N} - \frac{1}{K_{Equi}} \frac{f_{C_5H_{10}NH}}{f_{H_2}^2} \right) \\ r_{PP \rightarrow PA} = k_{PP} K_{PP-PPH} K_{PP} \mu f_{C_5H_{10}NH} C_*^2 \end{array} \right\}$$

- Modification for site balances

$$\left\{ \begin{array}{l} \delta = 1 + K_P f_{C_5H_5N} + K_{PP} f_{C_5H_{10}NH} + K_{NH_3} f_{NH_3} \\ \quad + K_{Solvent} f_{Solvent} + K_{PentylPP} f_{PentylPP} \\ \mu = K_{H_2S} f_{H_2S} + K_{H_2} f_{H_2} \end{array} \right\}$$

- Accounting for additional response, pentyl piperidine
 - Two possible reaction networks
 1. 2 Piperidine \rightarrow 1-Pentylpiperidine
 2. Piperidine + Pentylamine \rightarrow 1-Pentylpiperidine

Liquid phase modelling



- 1) Gas phase kinetics
- 2) Gas phase kinetics
- 3) Relative pentylamine reaction rate
- 4) Hydrogenolysis of 1-pentylpiperidine

Pentyl amine hydrogenolysis

$$r_{PA \rightarrow C5} = k_{PA} K_{PA-PAH} K_{PA} \mu f_{C_5H_{11}NH_2} C_*^2$$

Disproportionation of PP and PA

$$r_{PA+PP \rightarrow \text{PentylPP}} = k_{PA+PP} K_{PP} K_{PA} \sqrt{\frac{\mu}{\delta}} f_{C_5H_{10}NH} f_{C_5H_{11}NH_2} C_*^2$$

Conversion of PPP to PP + Pentane

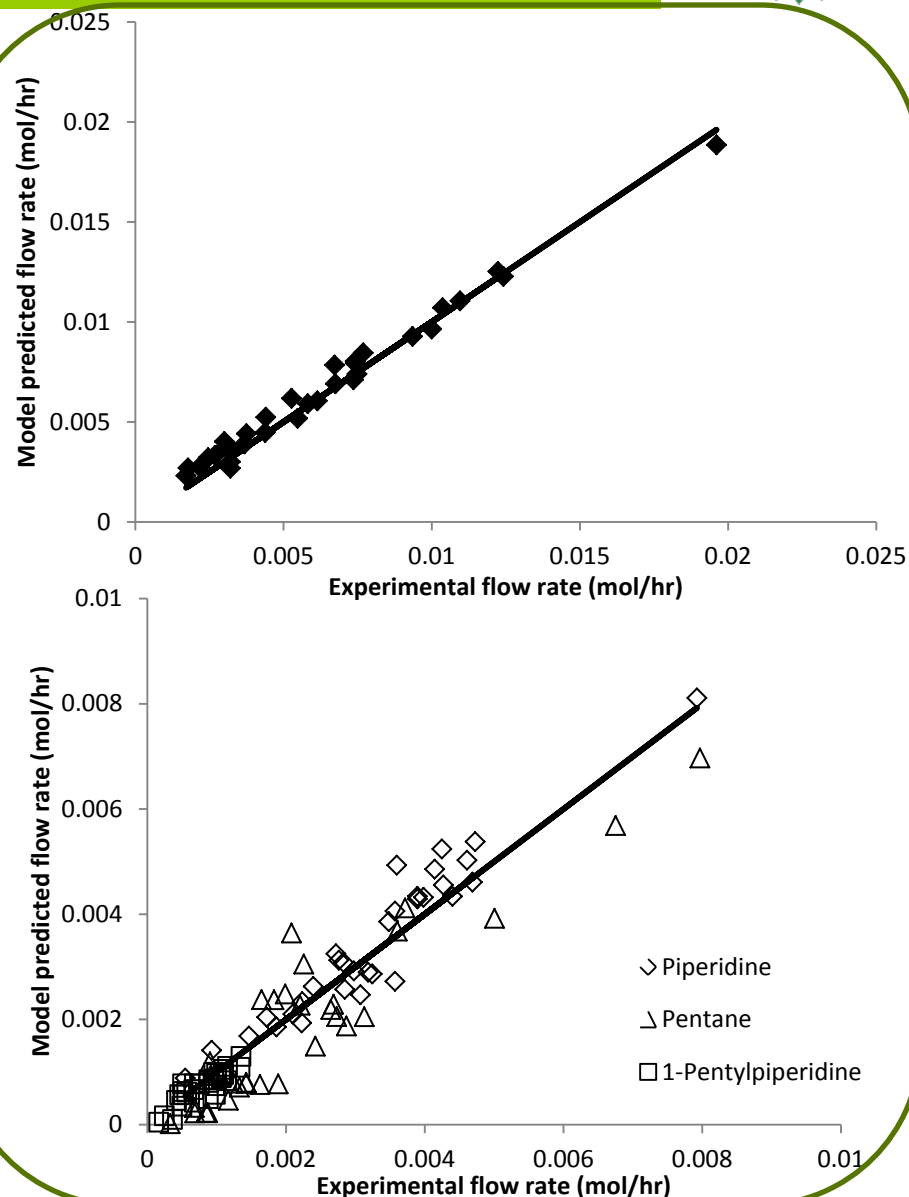
$$\begin{aligned}
 r_{\text{PentylPP} \rightarrow \text{PP} + C5} \\
 = k_{\text{PentylPP}} K_{\text{PentylPP}-\text{PentylPPH}} K_{\text{PentylPP}} \mu f_{\text{PentylPP}} C_*^2
 \end{aligned}$$

Liquid phase modelling : Results

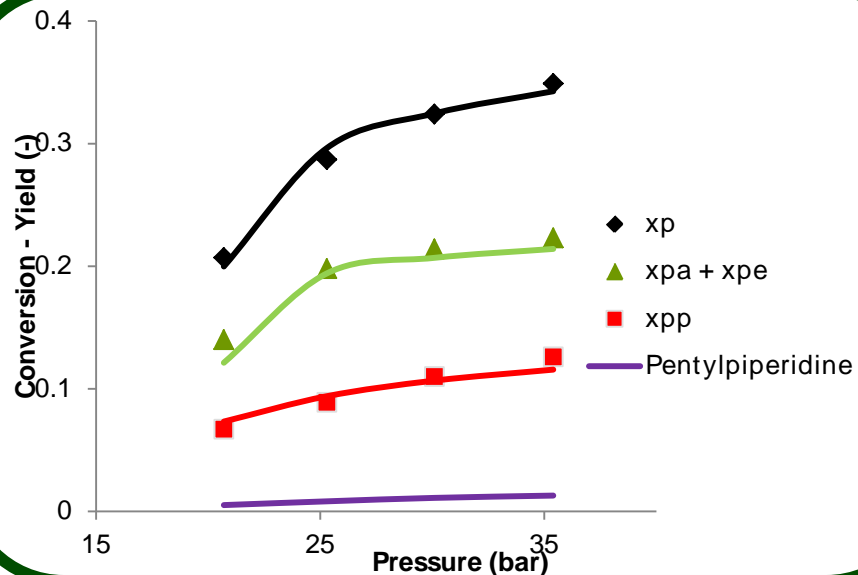
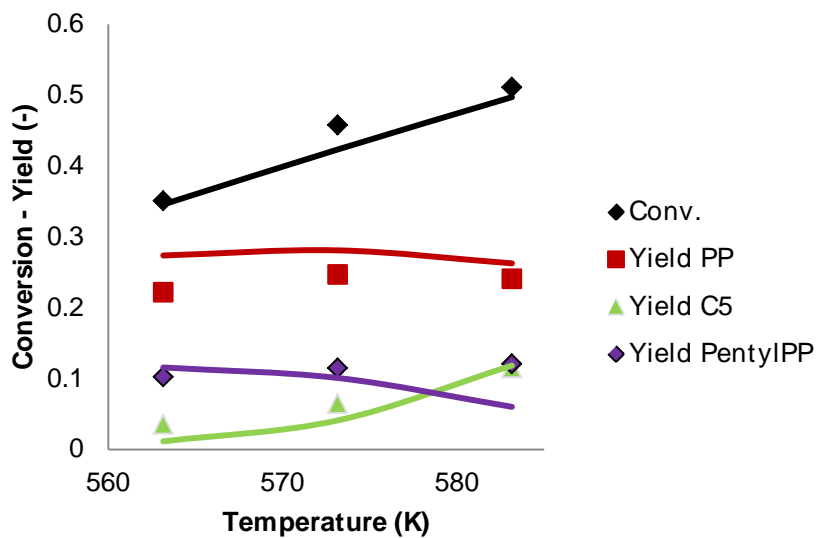
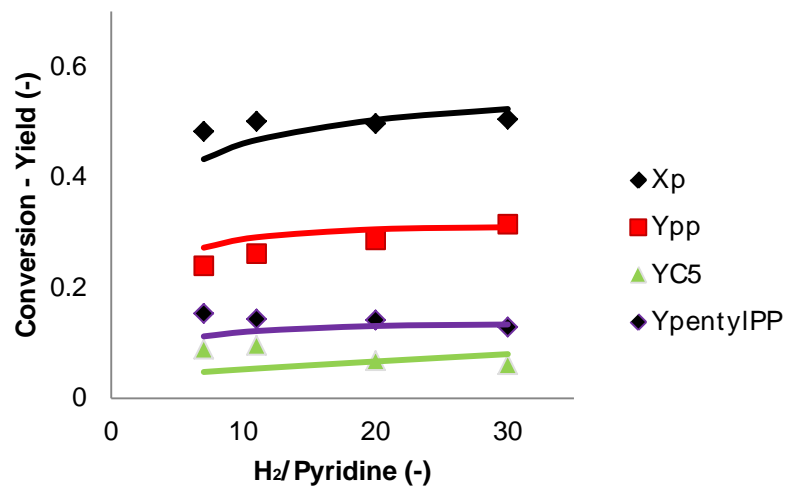
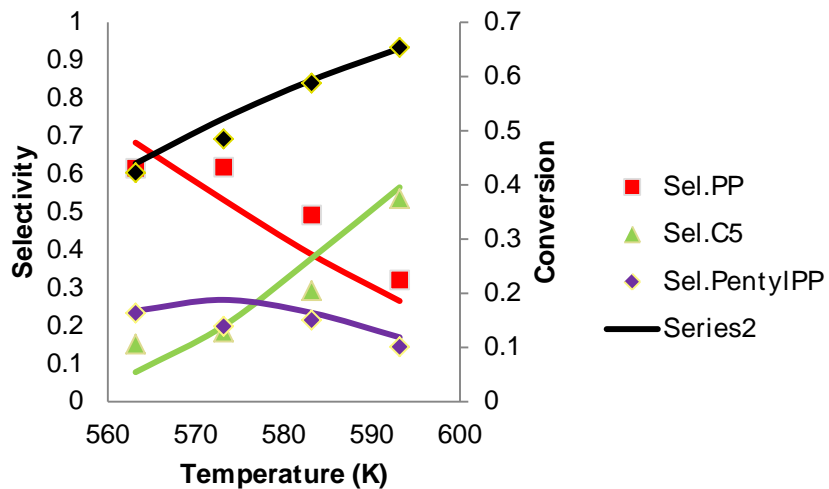


Parameter		Value
K_{solvent}	$-\Delta S$	98
	$-\Delta H$	37.6 ± 30.9
$K_{1\text{-pentylpiperidine}}$	$-\Delta S$	105
	$-\Delta H$	82.4 ± 29.1
k_{ratio}	k^*	0.05
$k_{\text{ratio}} = \frac{k_{\text{PA}^*}}{k_{\text{PA}+\text{PP}^*}}$	E_a	368.6 ± 115.9
$k_{\text{PentylPP} \rightarrow \text{PP}+\text{C5}}$	k^*	$1.07\text{E}+04$
	E_a	NS
C^*	-	1.81

Units $-\Delta S$ [J/mol-K], $-\Delta H$ [kJ/mol], k^* [mol/hr-kgcat], E_a [kJ/mol]



Liquid phase modelling : Results



Conclusions



- Proof of methodology with a case study on HDN
- Successful extension of gas phase kinetics to liquid phase reactions
 - Liquid phase to gas phase shown earlier
- A robust model that performed well in three phase and gas phase conditions
- First steps towards the extension to simulation to pilot plant data

Acknowledgements



Acknowledgements

- Ruben De Bruycker & Roeland Dieltiens
- Marko Djokic : 2D GC – MS Analysis
- Technical Staff (Ghent University)
- Colleagues at LCT and BP



Intrinsic kinetic regime verification



MT – Interface	Dimensionless Quantity	Limits	Reference
Gas – liquid	Carberry number for hydrogen	$Ca < 0.05/n$	Kapteijn et.al., 1993
Liquid – solid	Carberry number for hydrogen and pyridine	$Ca < 0.05/n$	Kapteijn et.al., 1993
Gas – solid	Carberry number for hydrogen and pyridine	$Ca < 0.05/n$	Kapteijn et.al., 1993
Intraparticle diffusion (catalyst side)	Weisz Modulus for hydrogen and pyridine	$\Phi < 0.08$ if $n > 0.5$	Weiss-Prater, 1954
Catalyst effectiveness		$> 95\%$	
ΔT at the L – S interface		$\Delta T_{L-S} < 0.63 \text{ K}$ $\Delta T_{int} < 0.63 \text{ K}$	Mears, 1971



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