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Temperature Stabilisation in Fischer-Tropsch Reactors using Phase Change Materials (PCM)

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Presentation Outline

- Background
- Research Objective
- Phase Change Materials(PCM)/PCM in Chemical Reactors
- Methodology and Mathematical Modelling
- Results and Discussion
- Conclusions and Future work

Background

- Conventional forms of energy are becoming increasingly scarce
- About US$100boe (~ 4.5 trillion MJ energy; ~265 MMt CO_2) was wasted through flared gas in 2011 and approximately7000tscf remained **stranded** globally as at 2011. (1,2)
- Small scale (<20bbl/day) reactors/mobile bio-refineries for production of **on-demand**, synthetic liquid fuels from diverse, under-utilised , local resources (including biomass) is fast becoming an emerging development area.
- The Fischer-Tropsch Synthesis (FTS) is one of the favoured Gas-to-Liquid (GTL) technologies. Its high exothermicity and sensitivity of product selectivity to temperature constitute the main challenge in FT reactor design.
- Phase Change Materials (PCM) in conjunction with traditional cooling systems is proposed as a means of intensifying and improving heat transport.

1. www.bp.com/content/dam/pdf/Statistical-Review-2012
2. www.worldbank.org/en/news/2012/07/03world-bank-sees-warning-sign-gas-flaring-increase

Objectives

- Brief introduction to the Fischer-Tropsch Synthesis (FTS)

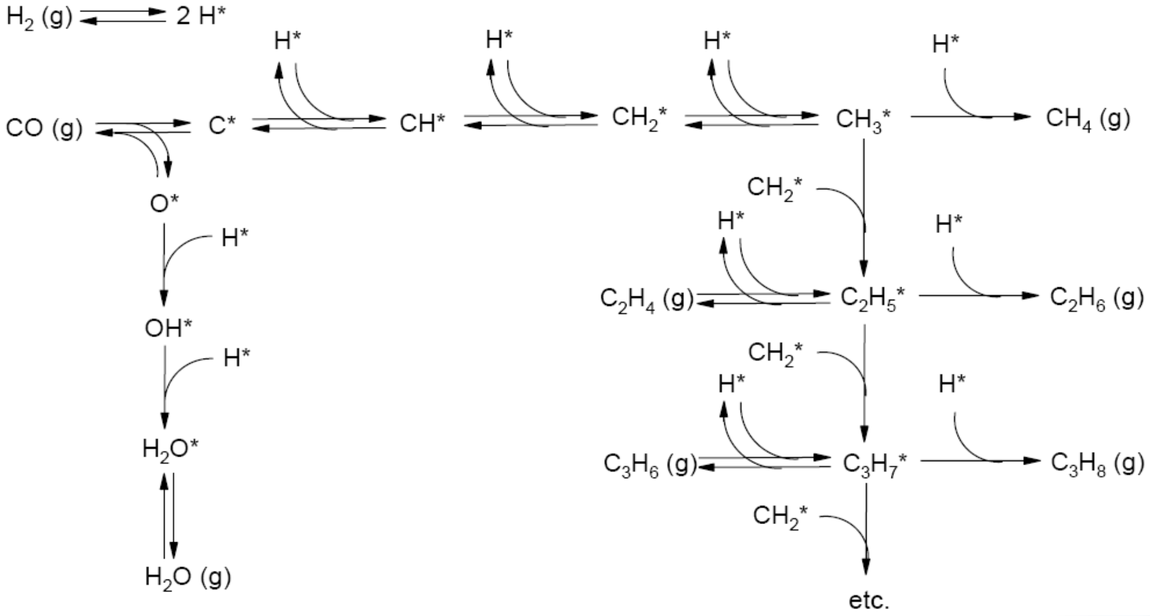
- Examine the concept of intensifying the heat transport system and regulation the temperature of a fixed bed FT reactor using phase change material (PCM). As well, to consider the effect of this increased temperature control on the spectrum of products emerging from the reactor

- Present a 2D-pseudo-homogeneous , steady state mathematical model and findings

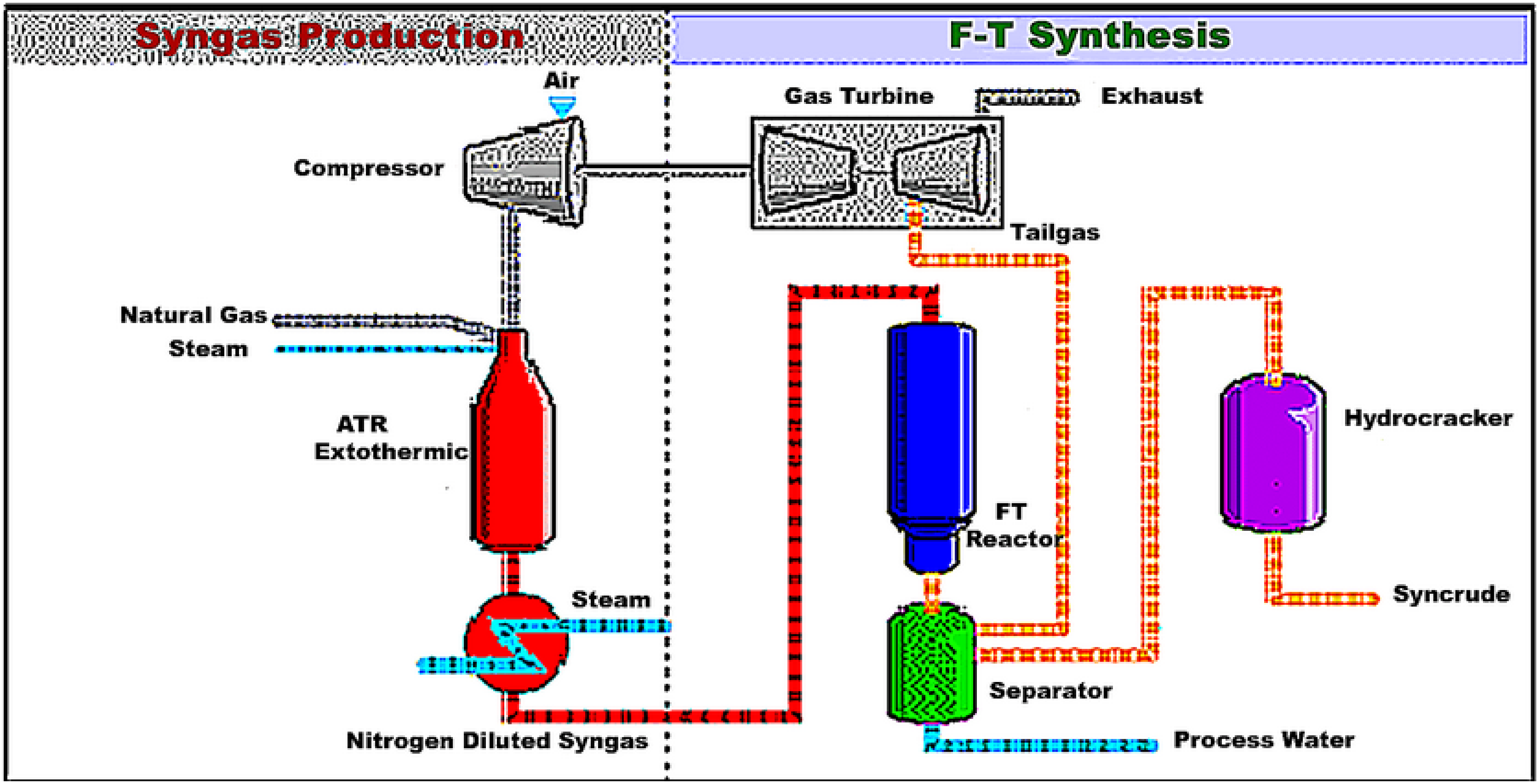
Fischer Tropsch Synthesis

- Refers to the aggregate of simultaneous, surface polymerisation reactions, occurring in-situ active catalyst sites (Ni, Fe, Co, Ru) to produce hydrocarbons from molecules of CO and H_2 (synthesis gas). Low Temperature FT (~200-250^{o}C) and High Temperature FT (~300-350^{o}C)

- Carbide mechanism: Dissociative adsorption of H_2 and CO



Process Flow Diagram



Source: Wikipedia

FT Product Distribution

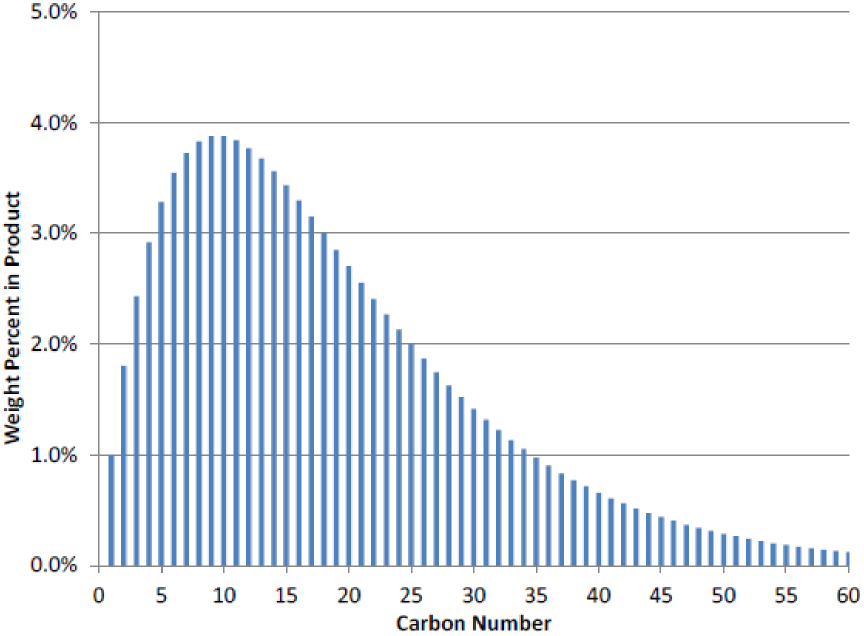
- Ideal Anderson-Schluz-Flory (ASF) distribution

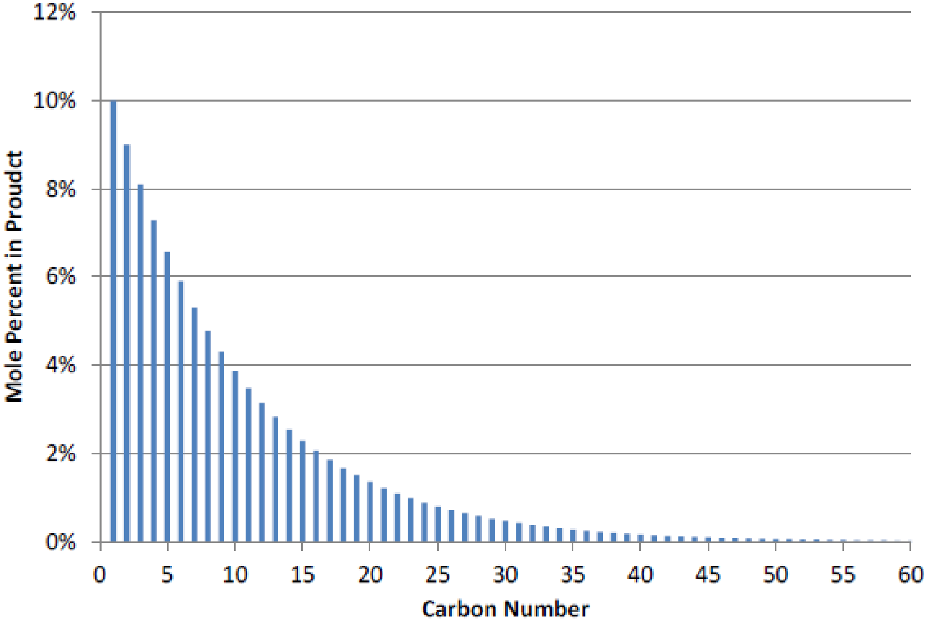
$$x_n = (1-\alpha) \times \alpha^{n-1}$$

α = $(0 \leq \alpha \leq 1)$ carbon-chain growth probability

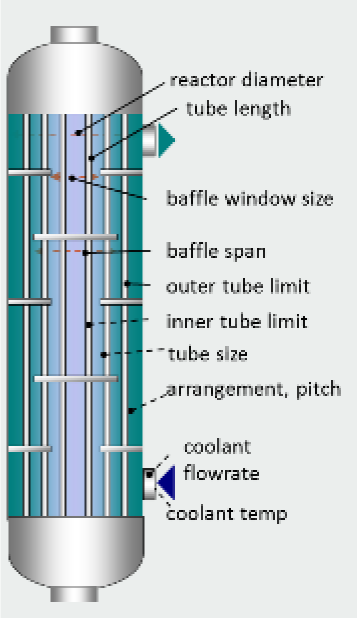
n = carbon number

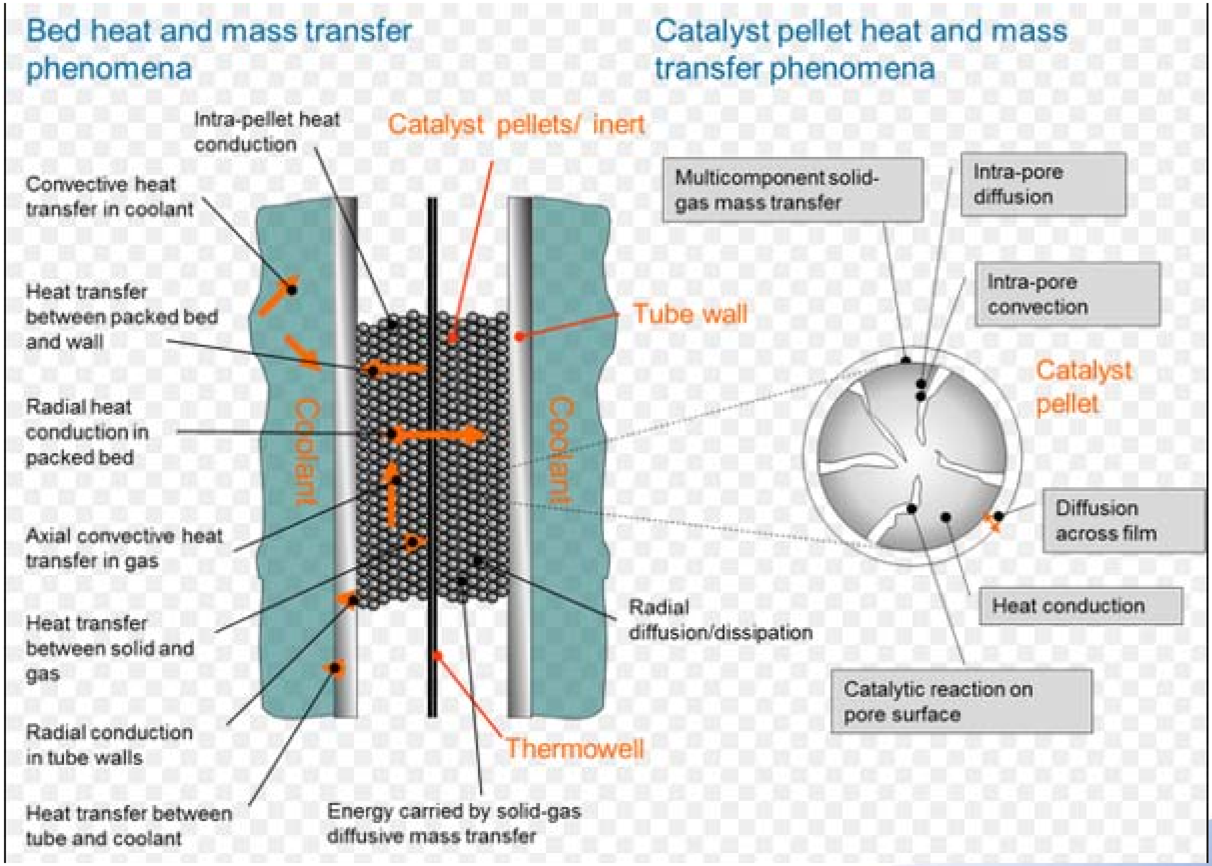
x_n = mass fraction





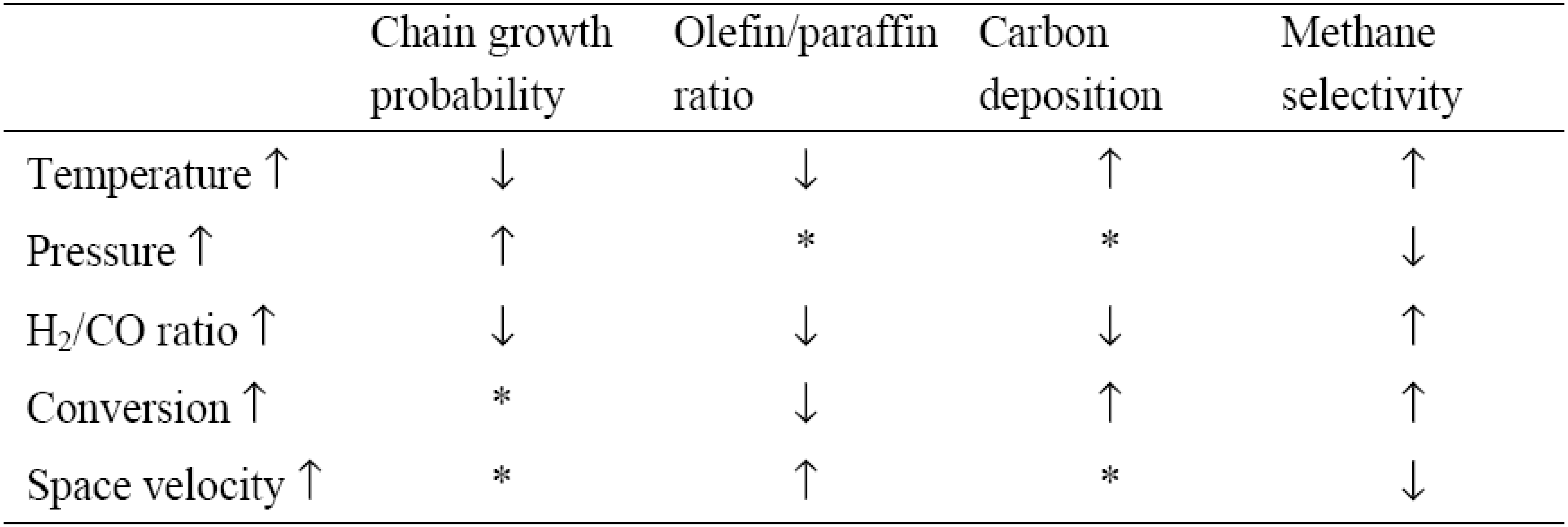
Fixed Bed Reactor (FBR)





PSE gproms www.psenterprise.com/gproms/aml/fbcr (accessed: 20/05/2014)

Effects of Process Conditions



	Chain growth probability	Olefin/paraffin ratio	Carbon deposition	Methane selectivity
Temperature ↑	↓	↓	↑	↑
Pressure ↑	↑	*	*	↓
H_2/CO ratio ↑	↓	↓	↓	↑
Conversion ↑	*	↓	↑	↑
Space velocity ↑	*	↑	*	↓

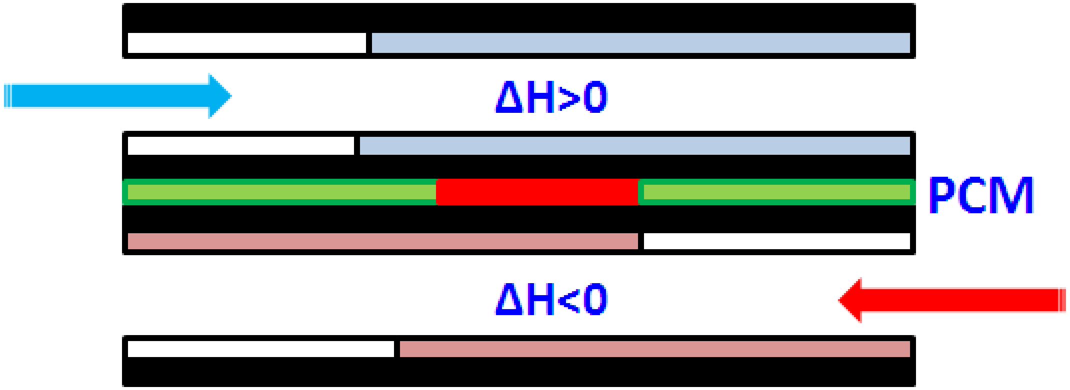
↑ increases ↓ decreases * Complex relationship

Note: Temperature increase affects process adversely on all fronts.

Phase Change Material (PCM)

- Provides an **isothermal sink** into which the enthalpy of reaction can be dissipated
- The melting-solidification cycles, **with enthalpy of fusion at constant temperature**, cause the PCM to act as an energy storage buffer/ thermal flywheel, mitigating temperature excursions
- PCM chosen so that phase transition temperature lies between maximum nominal temperature and maximum safe operating temperature
- Micro-encapsulated to prevent contamination or agglomeration. Micro-nano-size ensures rapid melting and mitigation of thermal runaway.
- Works as part of a hierarchical cooling system of control to produce **rapid response to temperature rise**.
- Packed closely with catalyst in a fixed bed to act as a distributed controller.

PCM in Chemical Reactors



Kinetics and Thermo-chemistry

- **Generic FTS:**

$CO + 2H_2 = (-CH_2-) + H_2O$ $\Delta_R H^{\theta}_{298K} = -152 \frac{kJ}{mol}$

$$r_{m,H_2,FT} = -\frac{k_{m,H_2,eff,FT}}{1 + 1.6 \frac{c_{H_2O}}{c_{CO}}} \cdot c_{H_{2,g}}$$

- **Methane synthesis:**

$CO + 3H_2 = CH_4 + H_2O$ $\Delta_R H^{\theta}_{298K} = -206 \frac{kJ}{mol}$

$$r_{m,H_2,M} = -k_{m,H_2,eff,M} \cdot c_{H_{2,g}}$$

- **Water-gas-shift reaction:**

$CO + H_2O = CO_2 + H_2$ $\Delta_R H^{\theta}_{298K} = -41 \frac{kJ}{mol}$

$$r_{m,H_2,WGS} = -k_{m,H_2,eff,WGS} \cdot c_{H_2O_g}$$

Mathematical model (I)

- Material Balance:

$$\rho_f u_s . \frac{\partial w_j^f}{\partial z} = -\rho_f . w_j . \frac{\partial u_s}{\partial z} - w_j u_s . \frac{\partial \rho_f}{\partial z}$$

$$+ D_{er} . \left(\frac{\partial \rho_f}{\partial r} . \frac{\partial w_j^f}{\partial r} + \frac{\rho_f}{r} . \frac{\partial w_j^f}{\partial r} + \rho_f . \frac{\partial^2 w_j^f}{\partial r^2}\right) + r_j M_j . \rho_b^{cat}$$

- Energy Balance:

$$\rho_f . u_s . C_p^f . \frac{\partial T^f}{\partial z} = \kappa_{er} . \left(\frac{1}{r} . \frac{\partial T^f}{\partial r} + \frac{\partial^2 T^f}{\partial r}\right)$$

$$- \rho_b^{cat} . \sum r_i . (\Delta_R H_i)$$

Whence,

$$\sum r_i . (\Delta_R H_i) = r_{m,H_2,FT} . (\Delta_R H_{FT}) + r_{m,H_2,M} . (\Delta_R H_M)$$

$$+ r_{m,H_2,WGS} . (\Delta_R H_{WGS}) - r_{PCM} . (\Delta_{fus} H_{PCM})$$

Mathematical model (II)

- Ergun's equation (Momentum Balance):

$$\left(\frac{\rho D_p}{G^2}\right).\left(\frac{\varepsilon^3}{1\text{-}\varepsilon}\right)\frac{dP}{dz} = 150.\frac{(1-\varepsilon)}{\left(\frac{D_p.G}{\mu}\right)} + 1.75$$

- Ideal gas EOS:

Type equation here.

$$\frac{\partial \rho_f}{\partial z} = \frac{MW}{R}\cdot\left(\frac{1}{T^f}\cdot\frac{\partial P}{\partial z} - \frac{P}{(T^f)^2}\cdot\frac{\partial T^f}{\partial z}\right)$$

- Effective Heat Capacity:

$$C_{p(PCM)} = \begin{cases} C_{p(PCM)s} & T < T_m \\ C_{p(PCM)s} + \dfrac{\Delta_{fus}H}{\Delta T} & T_m \leq T \leq (T_m + \Delta T) \\ C_{p(PCM)l} & T > (T_m + \Delta T) \end{cases}$$

Mathematical model (II)

- **Temperature dependent properties of PCM (melt fraction: *0≤ϕ ≤1*):**

$$\kappa_{PCM}(T) = \kappa_{PCMs}(1-\varphi) + \kappa_{PCMl} \times \varphi$$

$$\rho_{PCM}(T) = \rho_{PCMs}(1-\varphi) + \rho_{PCMl} \times \varphi$$

- **Pseudo-homogeneous fluid-catalyst-PCM system (*ω* = weight fraction of PCM):**

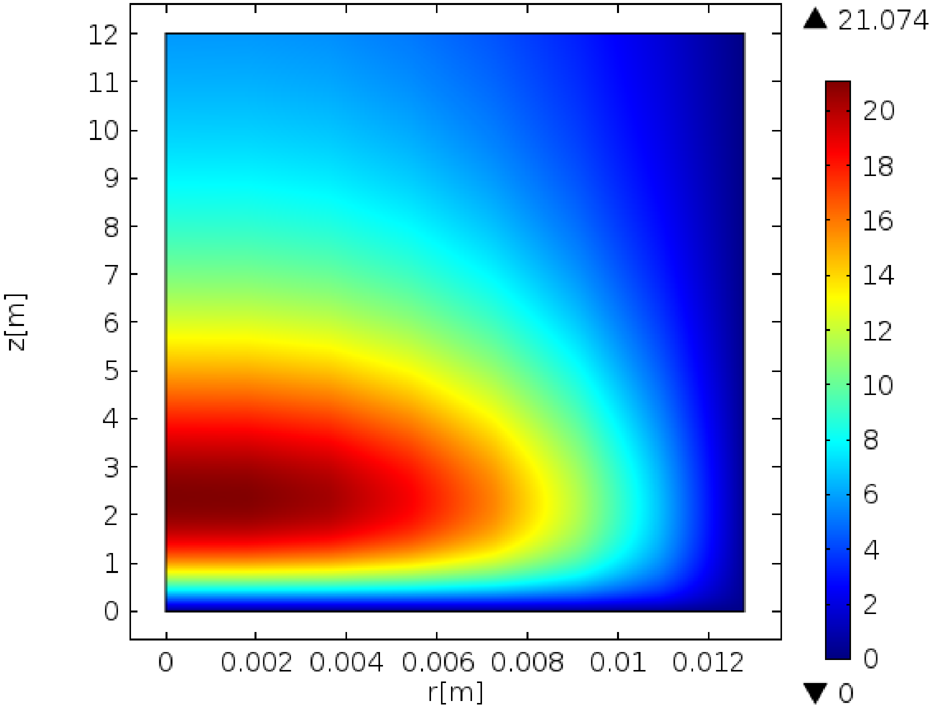
$$\kappa_{f,cat,PCM} = \frac{1}{(\omega+1)}.\kappa_{f,cat} + \frac{\omega}{(\omega+1)}.\kappa_{PCM}(T)$$

$$\rho_{f,cat,PCM} = \frac{1}{(\omega+1)}.\rho_{f,cat} + \frac{\omega}{(\omega+1)}.\rho_{PCM}(T)$$

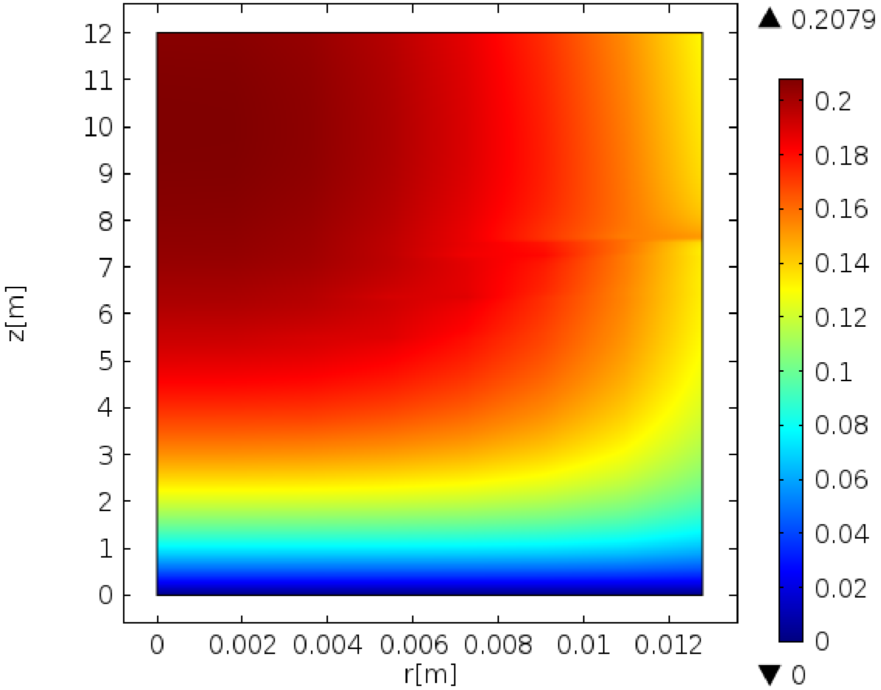
$$C_{p\,f,cat,PCM} = \frac{1}{(\omega+1)}.C_{p\,f,cat} + \frac{\omega}{(\omega+1)}.C_{p\,PCM}(T)$$

Results

- All data taken from and verified against modelling/experimental work of Jess and Kern (2009)



Non-PCM regulated reactor

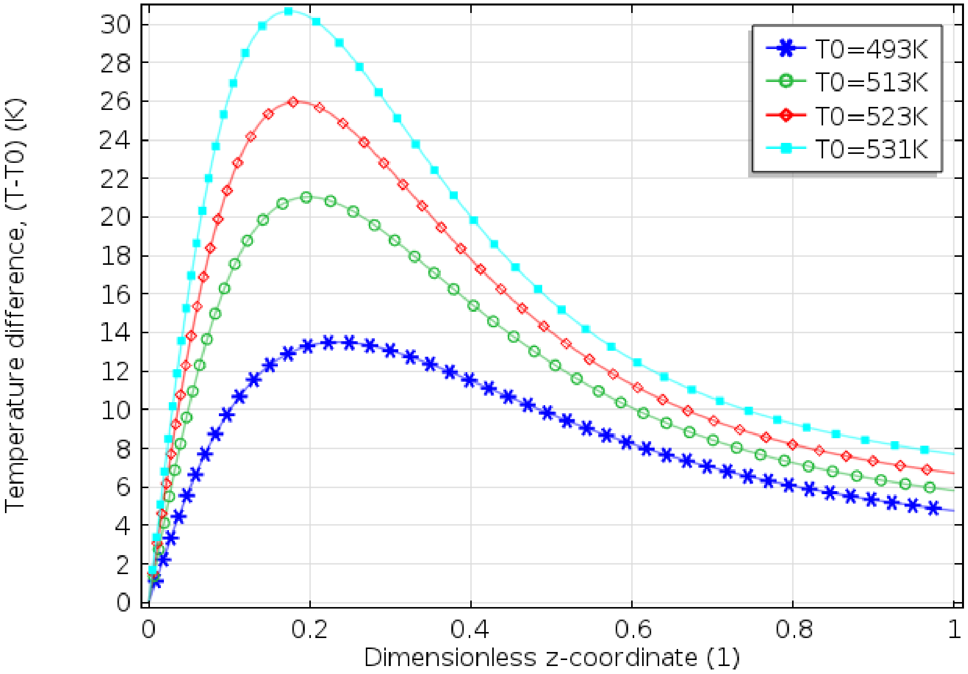


PCM regulated reactor

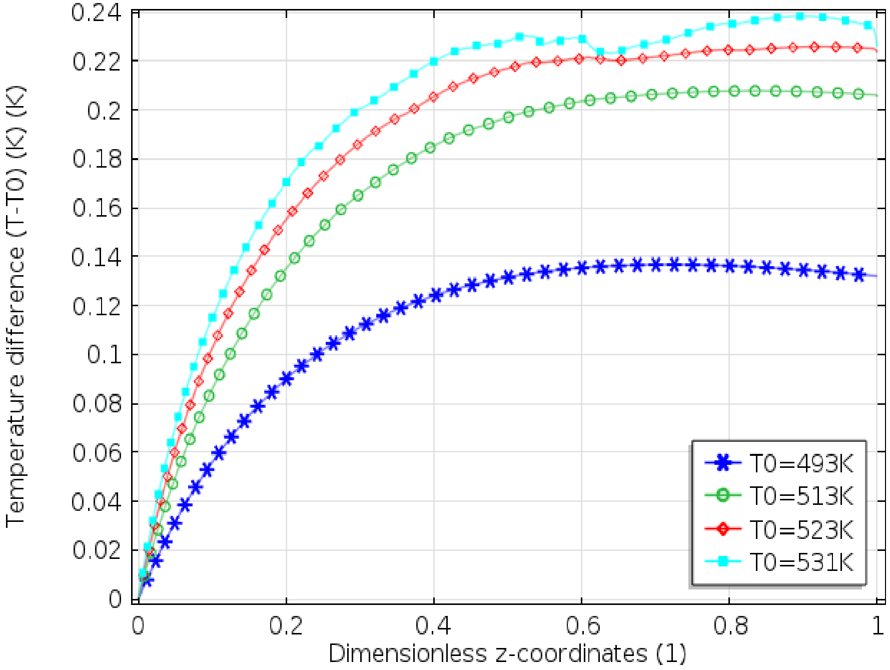
Jess A., Kern C. Modelling of Multi-tubular Reactors for Fischer-Tropsch Synthesis Chemical Engineering Technology 2009

Results

- Effect of varying inlet temperature



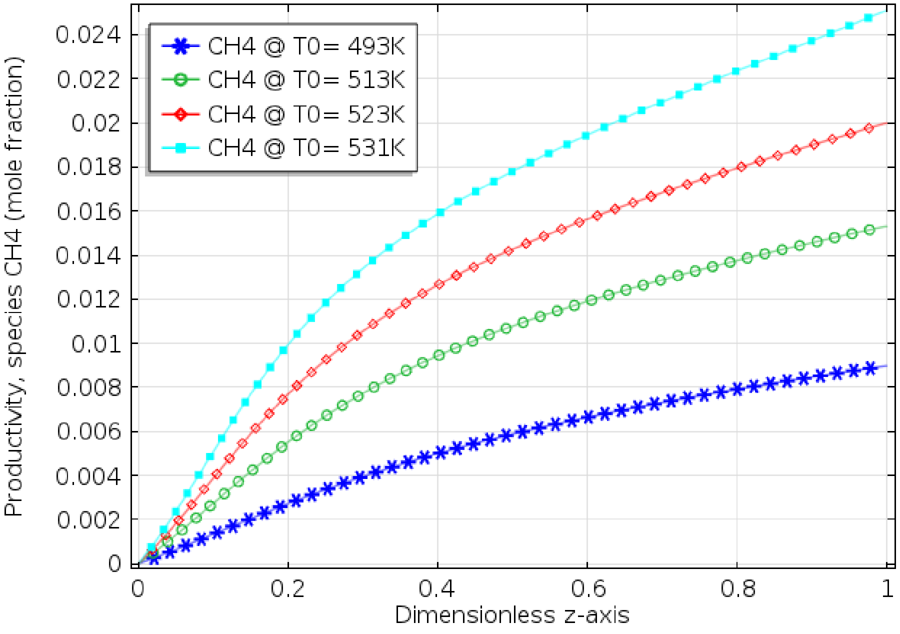
Non-PCM regulated reactor



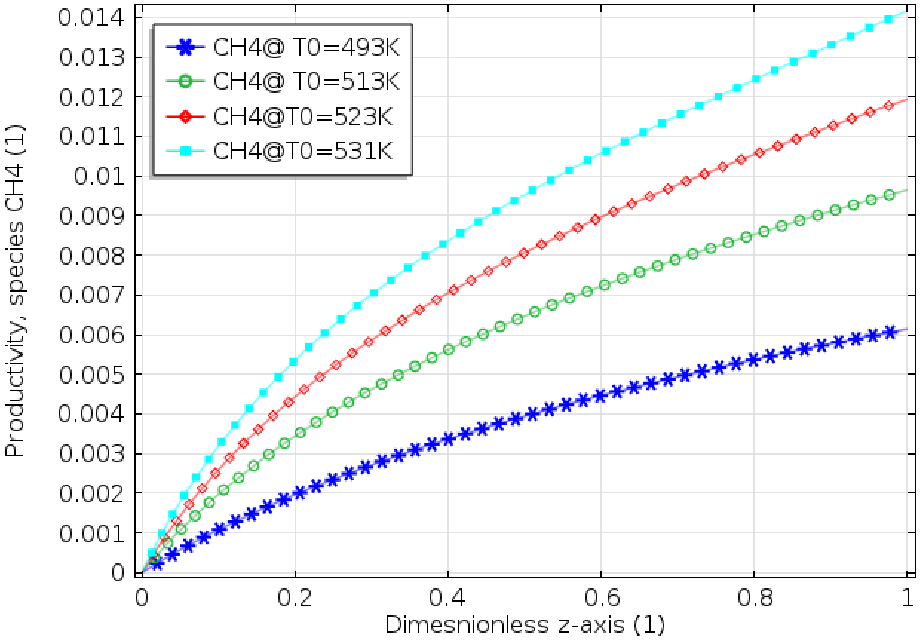
PCM regulated reactor

Results

- Effect of varied inlet temperature on methane productivity



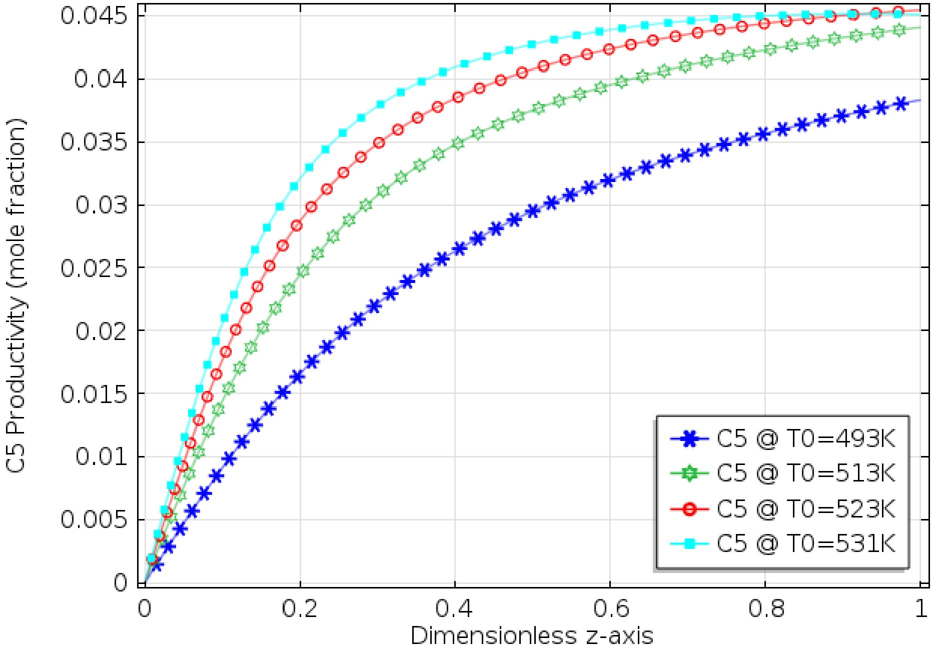
Non-PCM regulated reactor



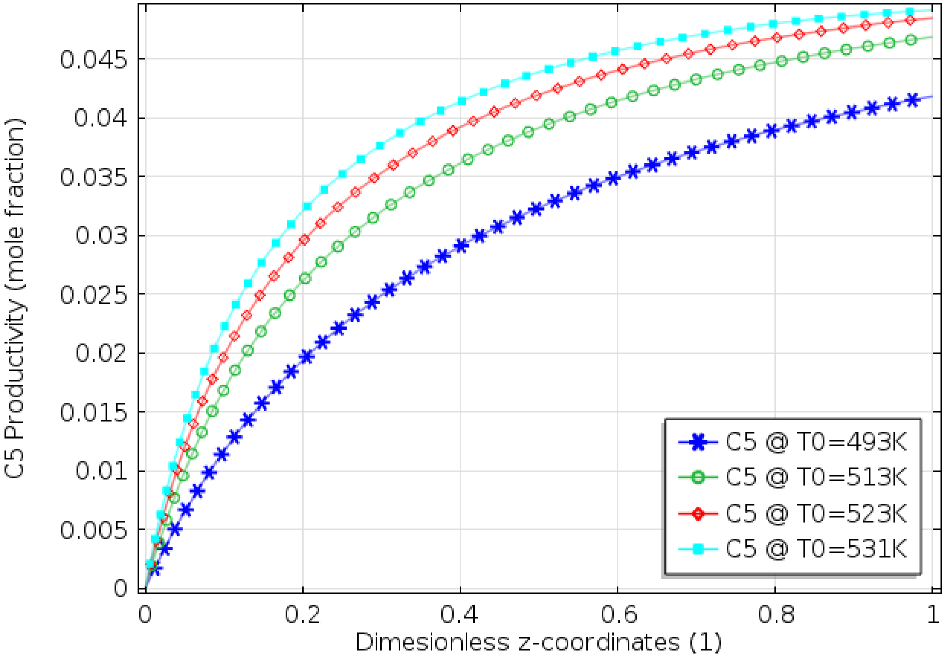
PCM regulated reactor

Results

- Effect of varied inlet temperature on C5+ productivity



Non-PCM regulated reactor



PCM regulated reactor

Conclusion

- 2D pseudo-homogeneous, steady state model has been presented
- The concept of PCM in reactors (FT) has been examined
- The delay in temperature rise of PCM keeps the reaction bed within a narrow optimum temperature range and thus maintains a desirable product selectivity window
- The potential, rapid-response, distributed control capabilities of the PCM can be seen. Potential tuning parameters include mass fraction, melt time, etc.
- Catalyst supports in future may be impregnated with PCM to act as a temperature control buffer
- Future work will involve optimisation and experimentation.

Thanks for your attention.

Reaction Modelling Parameters

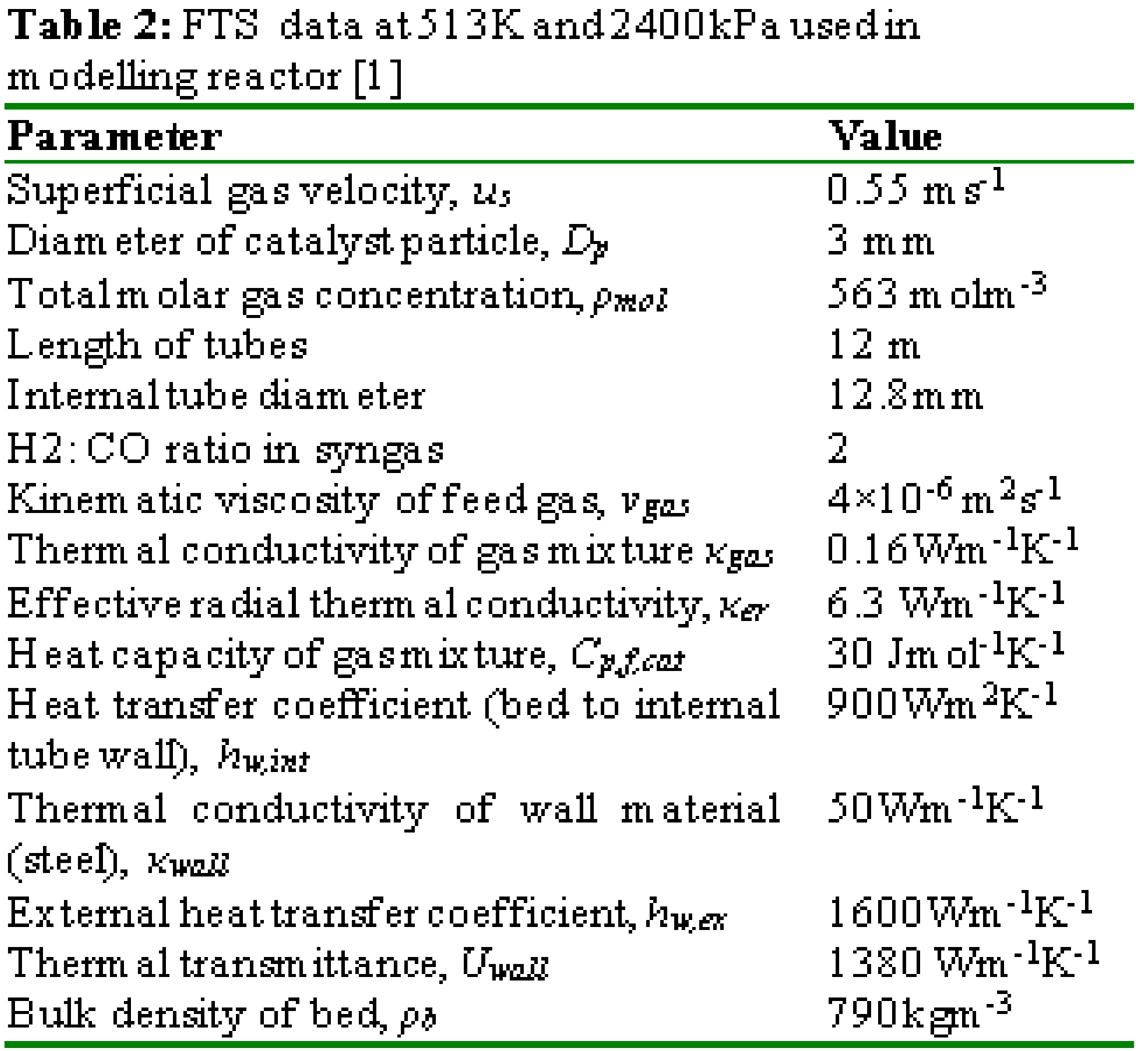


Table 2: FTS data at 513K and 2400kPa used in modelling reactor [1]

Parameter	**Value**
Superficial gas velocity, u_s	0.55 m s^{-1}
Diameter of catalyst particle, D_p	3 mm
Total molar gas concentration, ρ_{mol}	563 molm^{-3}
Length of tubes	12 m
Internal tube diameter	12.8mm
H2:CO ratio in syngas	2
Kinematic viscosity of feed gas, v_{gas}	4×10^{-6} m^2s^{-1}
Thermal conductivity of gas mixture κ_{gas}	0.16 $Wm^{-1}K^{-1}$
Effective radial thermal conductivity, κ_{er}	6.3 $Wm^{-1}K^{-1}$
Heat capacity of gas mixture, $C_{p,f,cat}$	30 $Jmol^{-1}K^{-1}$
Heat transfer coefficient (bed to internal tube wall), $h_{w,int}$	900 $Wm^{-2}K^{-1}$
Thermal conductivity of wall material (steel), κ_{wall}	50 $Wm^{-1}K^{-1}$
External heat transfer coefficient, $h_{w,ex}$	1600 $Wm^{-1}K^{-1}$
Thermal transmittance, U_{wall}	1380 $Wm^{-1}K^{-1}$
Bulk density of bed, ρ_b	790 kgm^{-3}

PCM Physical Properties

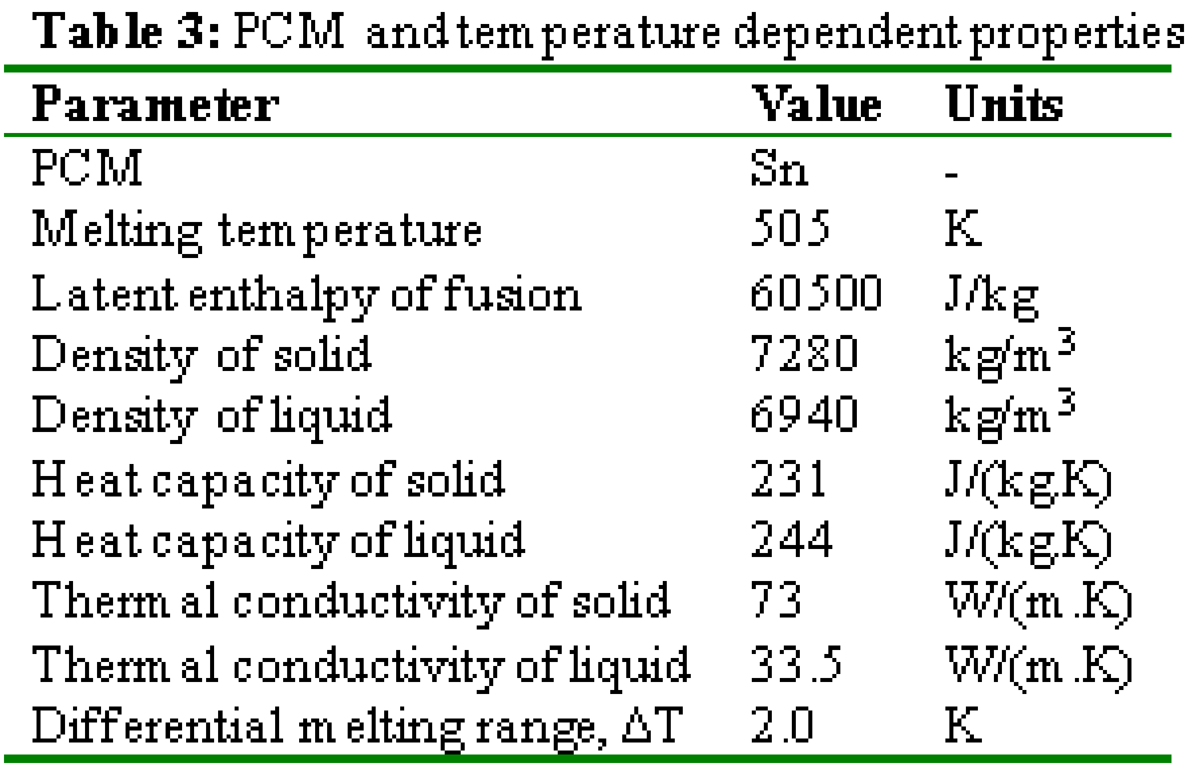


Table 3: PCM and temperature dependent properties

Parameter	**Value**	**Units**
PCM	Sn	-
Melting temperature	505	K
Latent enthalpy of fusion	60500	J/kg
Density of solid	7280	kg/m^3
Density of liquid	6940	kg/m^3
Heat capacity of solid	231	J/(kg.K)
Heat capacity of liquid	244	J/(kg.K)
Thermal conductivity of solid	73	W/(m.K)
Thermal conductivity of liquid	33.5	W/(m.K)
Differential melting range, ΔT	2.0	K