Experimental and kinetic study of (Trans)Esterification reactions on Lewatit K1221

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Introduction & scope

Esterification & Transesterification reactions play a key role in today's **biorefineries**. Conventionally, these reactions are performed using an acid or a base **homogeneous catalyst.**

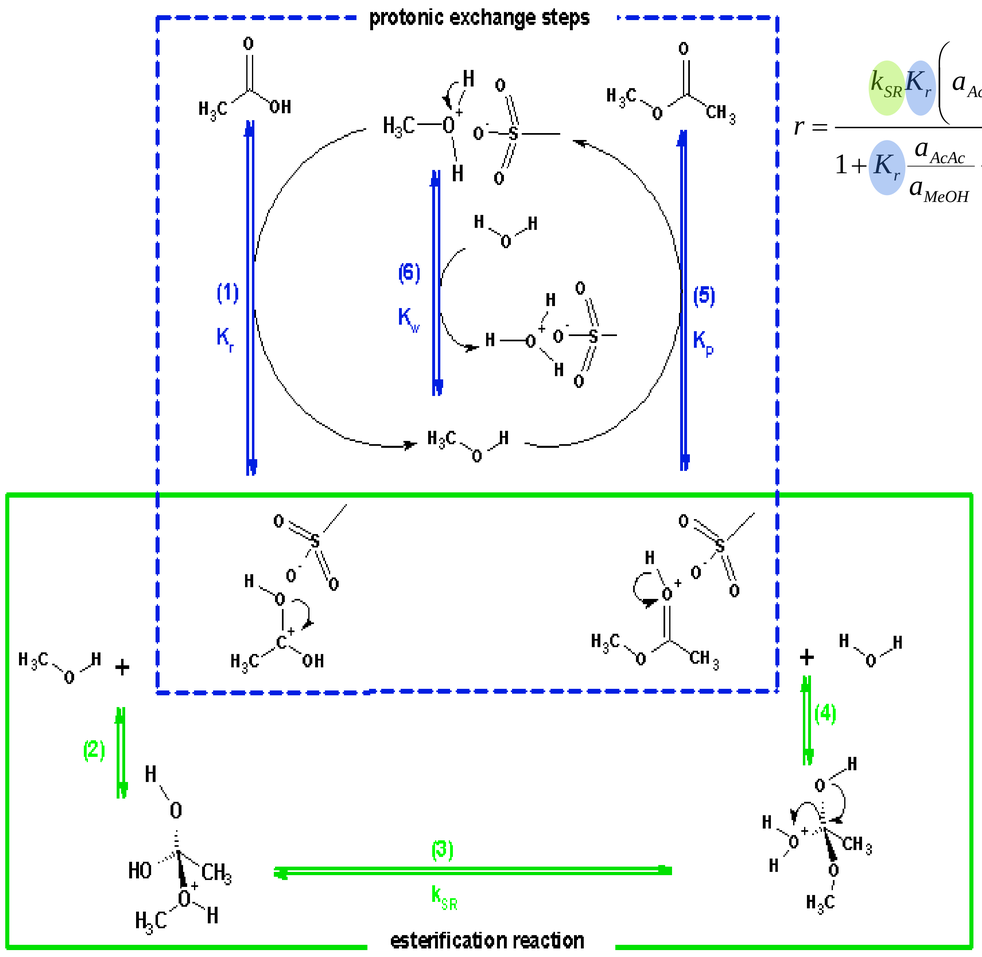
Heterogeneous catalysis
- **(+)** not dedicated catalyst separation
- **(+)** no purification.

} **acid ion-exchange resin** can catalyze → **esterification**, **transesterification**
- **(+)** ecofriendly
- **(+)** non corrosive
- **(+)** good stability
- **(+)** reusability
- **(!)** swelling in a polar solvent => determines the **accessibility** of its active sites => critical role in **reaction kinetics**

Esterification

Transesterification

Reaction Mechanism & Kinetic model

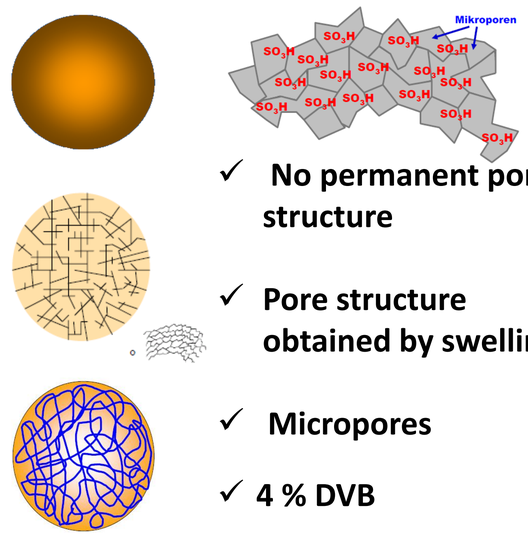


$$r = \frac{k_{SR}K_r\left(a_{AcAc} - \frac{1}{K_{eq}}\frac{a_{MeOAc}a_{H_2O}}{a_{MeOH}}\right)}{1 + K_r\frac{a_{AcAc}}{a_{MeOH}} + K_p\frac{a_{MeOAc}}{a_{MeOH}} + K_w\frac{a_{H_2O}}{a_{MeOH}}}$$

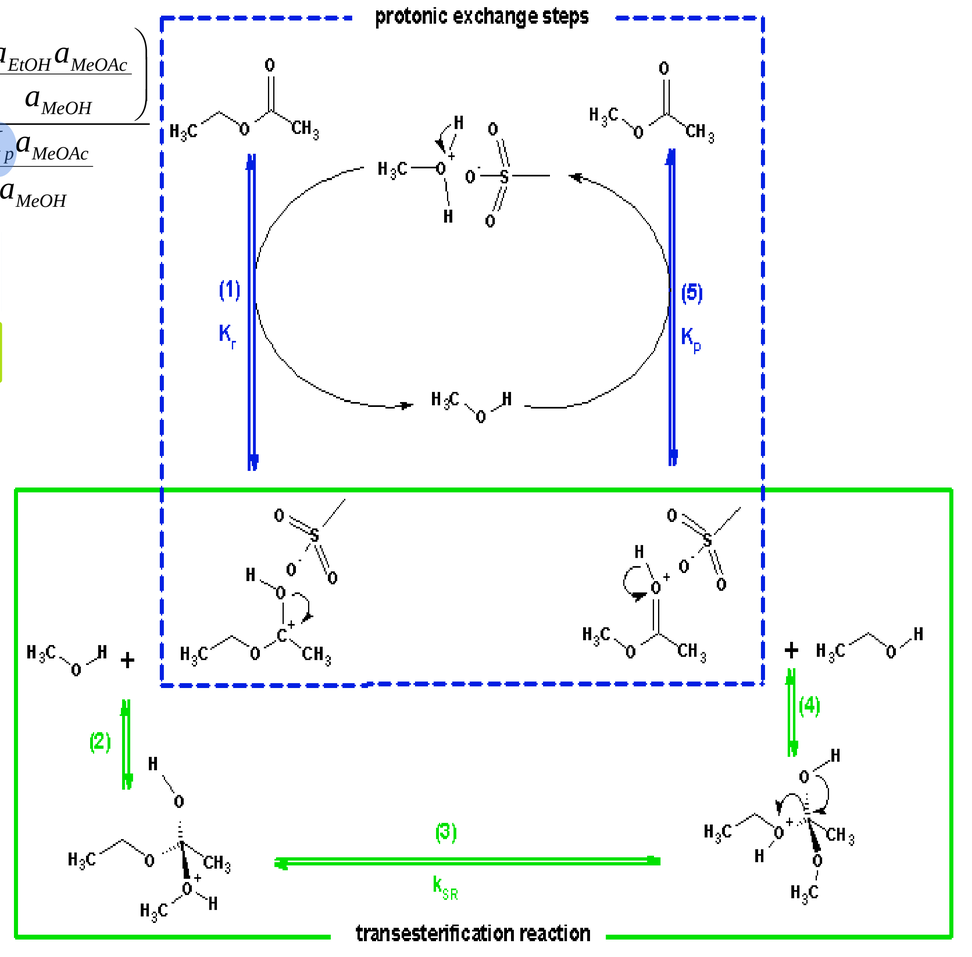
$$r = \frac{k_{SR}K_r\left(a_{EtOAc} - \frac{1}{K_{eq}}\frac{a_{EtOH}a_{MeOAc}}{a_{MeOH}}\right)}{1 + \frac{K_r a_{EtOAc}}{a_{MeOH}} + \frac{K_p a_{MeOAc}}{a_{MeOH}}}$$

Catalyst

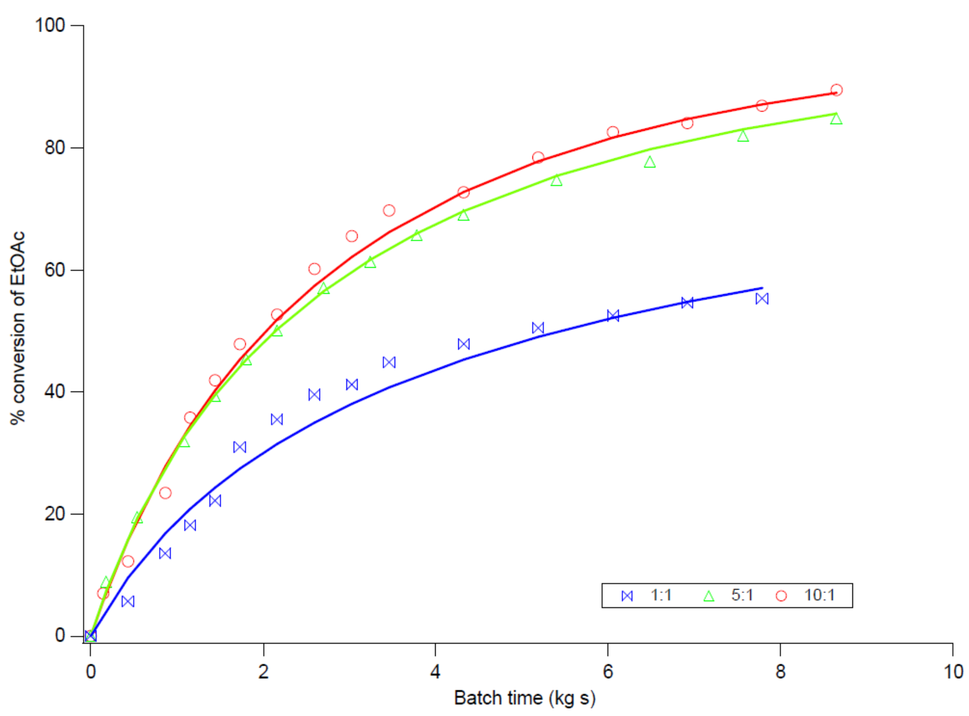
Lewatit K1221



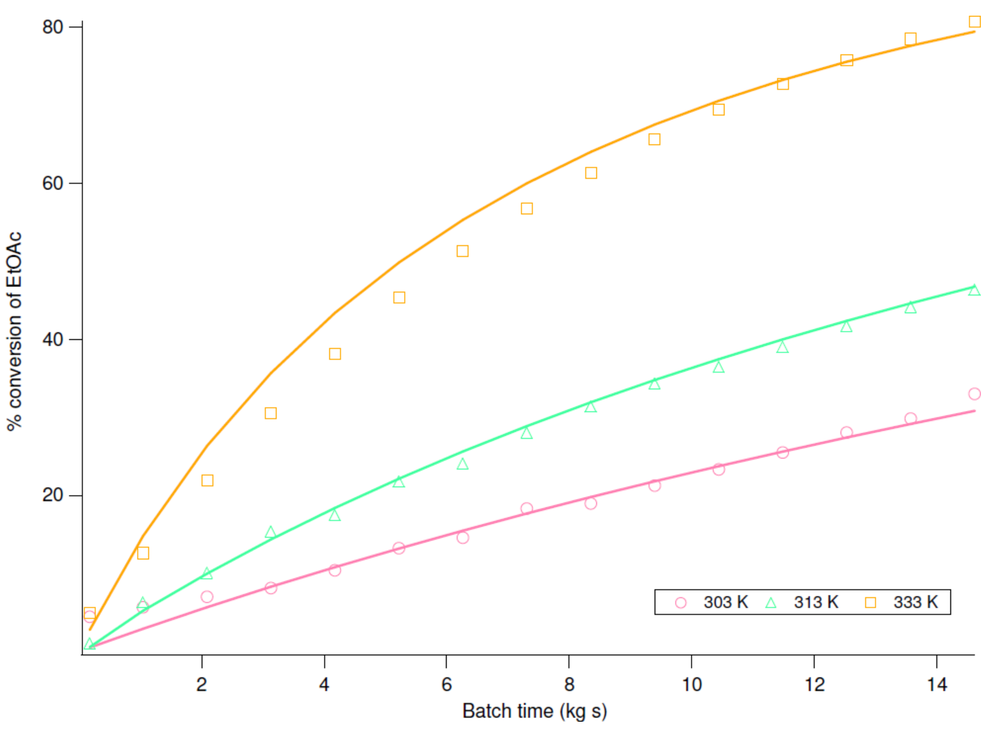
- ✓ **No permanent pore structure**
- ✓ **Pore structure obtained by swelling**
- ✓ **Micropores**
- ✓ **4 % DVB**



Modelling results



$k_{SR}(10^{-3} mol\ kg_{cat}^{-1} s^{-1})$	
50.8 ± 6.0	52.7 ± 0.3
$E_A(kJ\ mol^{-1})$	
46.1 ± 1.9	48.7 ± 0.9
K_r	
4.3 ± 0.3	1.2 ± 0.1
K_p	
0.0	4.9 ± 0.4
K_w	
7.9 ± 0.7	



Conclusions & perspectives

- ✓ **Temperature** and **initial molar ratio effect adequately modelled** with **proposed reaction mechanism**.
- ✓ In the mechanism are **all the acid sites covered** and is **sorption** expressed by an **exchange**.
- ✓ **Activation energy of 48 kJ mol^{-1}**, irrespective of the reaction type.
- ✓ **Unique set of exchange coefficients** for each reaction.
- ✓ **High value** of **ion-exchange coefficient K_w** shows the **inhibiting** effect of water on the esterification.
- ✓ For 333 K and initial molar ratio of 10:1, at **least 60 %** of the catalyst's **active sites** were covered by **methanol**

Acknowledgements