

Homogeneous Catalysts and Development of Solid Acid and Basic Catalysts for Continuous Production of Biodiesel

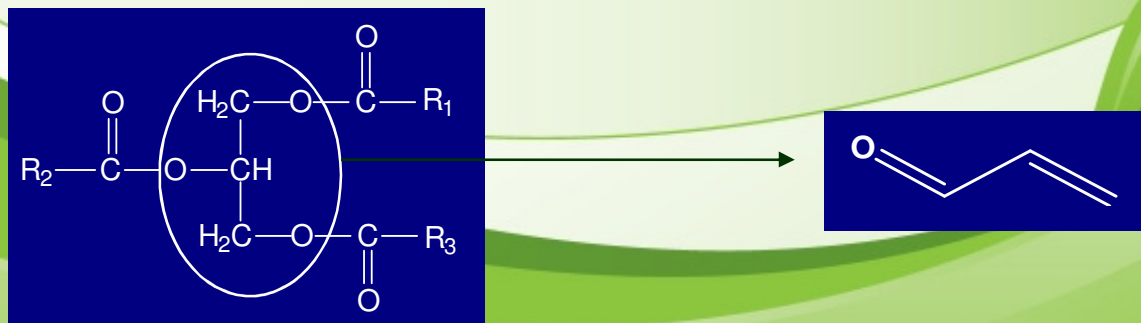
Prof. Dr. Ulf Schuchardt
Instituto de Química da Unicamp
CEP 13083-970, Campinas – SP
ulf@iqm.unicamp.br
Pesquisador Sênior do CNPq



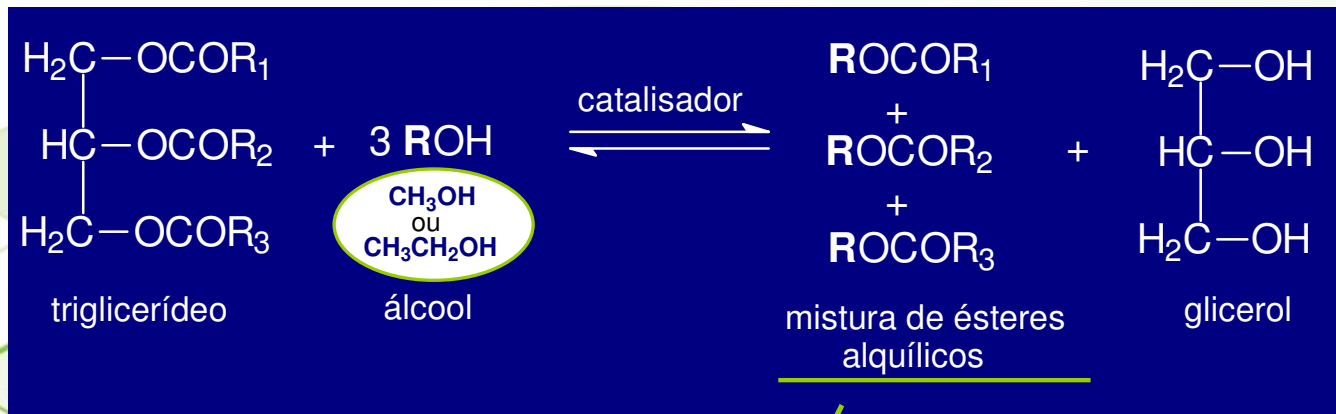
→ Vegetable Oils have a high calorific value and have no sulfur in their composition

However, the use of vegetable oils as fuel shows some strong disadvantages:

- ⊙ High Viscosity.
- ⊙ Incomplete Combustion.
- ⊙ Formation of coke deposits in the injection system.
- ⊙ Reduction of lubrication efficiency.
- ⊙ Obstruction of oil filter and injection system.
- ⊙ Reduction of engine durability.
- ⊙ Formation of acrolein by thermal decomposition of glycerol.



The transesterification of vegetable oils is of strategic importance for the energetic sector since the reaction of vegetable oils with short chain alcohols forms esters (biodiesel) which are a natural substitute for mineral diesel oil, as biodiesel and mineral diesel have similar characteristics.



Fuel for diesel engines (Biodiesel)

Biodiesel is no novelty for Brazil

- ➔ **1920:** First reference for the use of vegetable oils as fuel in diesel engines.
- ➔ **1950:** Studies on the use of different vegetable oils in 6 cylinder diesel trucks (Ministry of Agriculture)
- ➔ **1979/80 (Governments Geisel/Figueiredo):** ProÓleo
- ➔ **2003: Return of ProÓleo,** which is now called National Biodiesel Programme.

First Brazilian Patents

➔ **1980: Parente, E. J. S.**

First patent on the use of biodiesel as kerosene for aviation.

Parente, E. J. S; PI 8007957, 1980.

➔ **1982: Schuchardt. U.**

Prêmio Governador do Estado de São Paulo

Continuous reactor using organic heterogeneous catalysts for the transesterification of vegetable oils.

Schuchardt, U.; Lopes O. C; PI 8202429-4, 1982 .

➔ **1983: U. Schuchardt.**

Prêmio de Governador do Estado de São Paulo

Process for the preparation of methyl esters with organic catalysts and the rapid determination of the composition of fats and oils.

Schuchardt, U.; Lopes, O. C.; PI 8302366-6 1983.

Ethanol

Advantages

- Renewable.
- Brazilian production.
- None toxic.

Disadvantages

- Separation from glycerin more complex.
- Higher investment costs .

Methanol

Advantages

- Cheaper.
- Immediate separation from glycerin.
- Exportation fuel.

Disadvantages

- Toxic.
- Imported in Brazil.

Homogeneous Alkaline Catalysis

Catalysts : NaOH, KOH, RONA, ROK



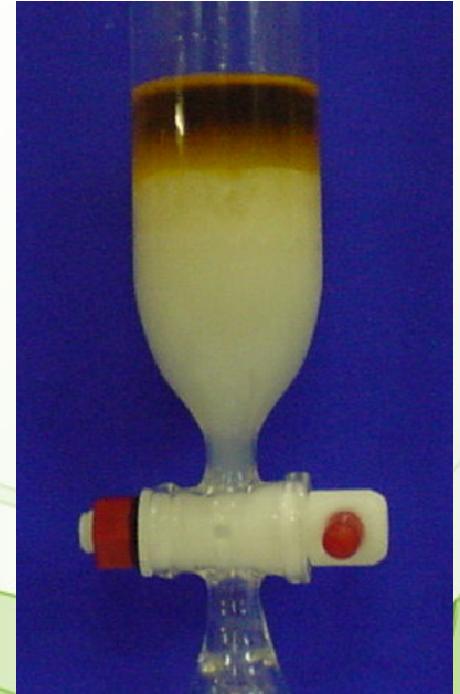
The homogeneous alkaline transesterification is a simple process which is widely used in industry.



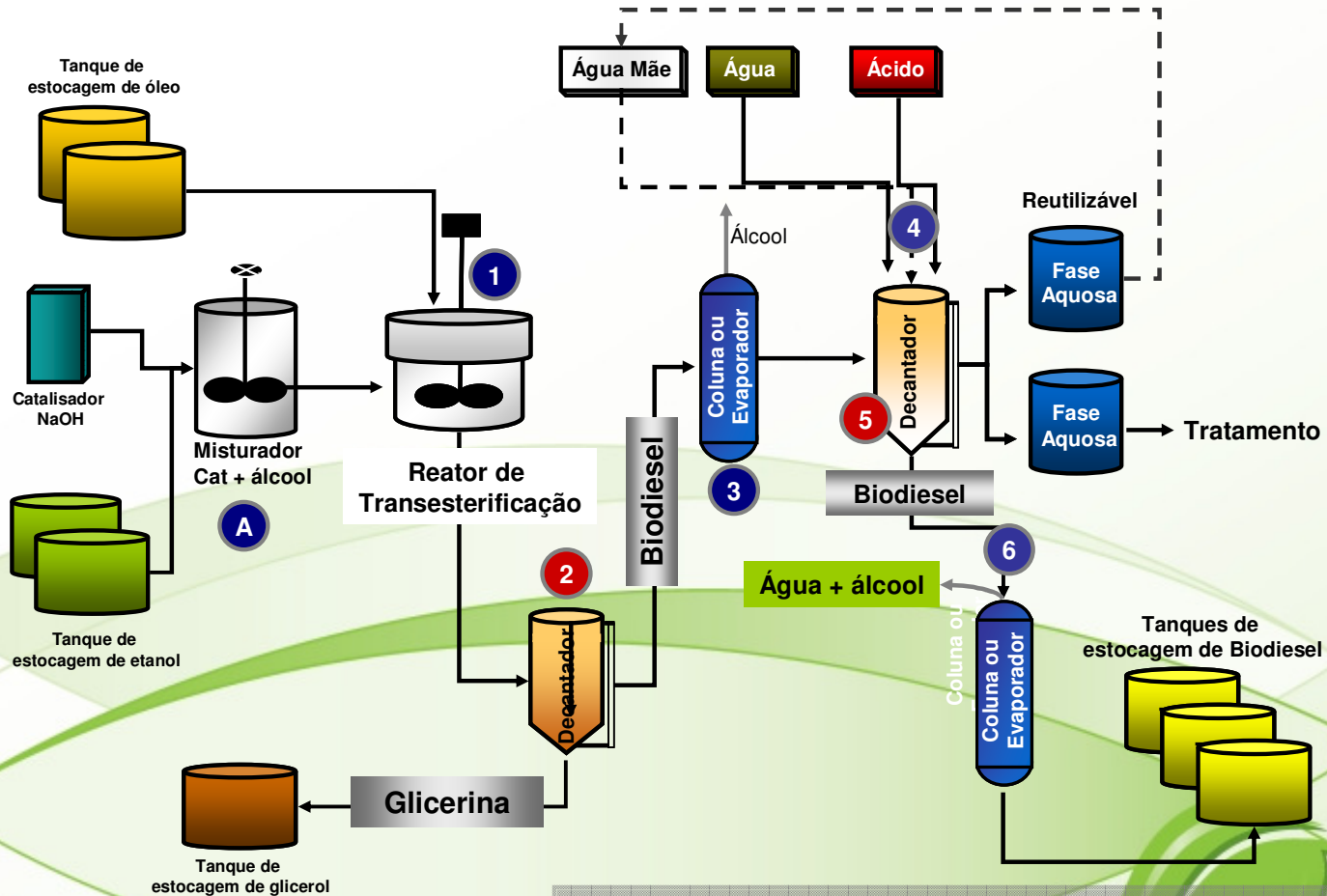
Critical points: efficiency of phase separation, specifically if ethanol is used. Purification of the products and by-products.



Development of better equipment for separation and purification of the products is necessary.



Industrial plant for the batch production of Biodiesel



Etapas

- A** Mistura do álcool com o Catalisador,
- 1** Transesterificação
- 2** Separação do biodiesel e glicerina
- 3** Recuperação do álcool
- 4** Lavagem do biodiesel
- 5** Eliminação de resíduos de catalisador e subprodutos
Separação do Biodiesel e água de lavagem
- 6** Secagem do biodiesel

➔ Homogeneous Catalysis

Catalyst and substrate are in the same phase.

Examples

- **Acids:** HCl, H₂SO₄, sulfonic acids

- **Bases:** Hydroxides, carbonates and alcoxides of Na or K.

R.M. Vargas, R. Sercheli, U. Schuchardt; *J. Braz. Chem. Soc.* 9 (1998) 199.

G. Vicente, M. Martínez, J. Aracil; *Bioresour. Technol.* 92 (2004) 297.

➔ Heterogeneous Catalysis

Catalyst and substrate are not in the same phase, which allows the easy separation of the catalyst after the reaction.

Examples

- **Acids:** Zirconia-alumina doped with tungsten.

S. Furuta, H. Matsuhashi, K. Arata; *Catal. Commun.* 5 (2004) 721.

- **Bases:** CaO, Ca(OMe)₂, Ba(OH)₂, Mg(OH)₂, CaCO₃

S. Gryglewicz; *Bioresour. Technol.* 70 (1999) 249.

G.J. Suppes, K. Bockwinkel, S. Lucas, J.B. Botts, M.H. Mason, J.A. Heppert; *J. Am. Oil Chem. Soc.* 78 (2001) 139.

Catalysts

Homogeneous basic

- 😊 Alkaline catalysts can be easily handled.
- 😊 Less corrosive than homogeneous acid catalysts.
- 😞 More steps to produce biodiesel.
- 😞 Higher production of residues due to neutralization of the catalyst, purification of the products and recuperation of the glycerin.

Heterogeneous acid

- 😊 Can be used for the transesterification of vegetable oils with a high content of free fatty acids.
- 😊 Significant reduction of purification steps.
- 😊 Easy reuse of the catalyst.
- 😊 No corrosion of the plant.
- 😊 Easy purification of the glycerin.
- 😞 Longer reaction times and higher temperature.
- 😞 More sophisticated industrial plants.

The presence of free fatty acids does not allow the synthesis of biodiesel using homogeneous basic catalysis.

Either the free fatty acids have first to be esterified or the oil has to be hydrolyzed to free fatty acids to then promote the conversion to biodiesel which implies in a larger number of reactions.

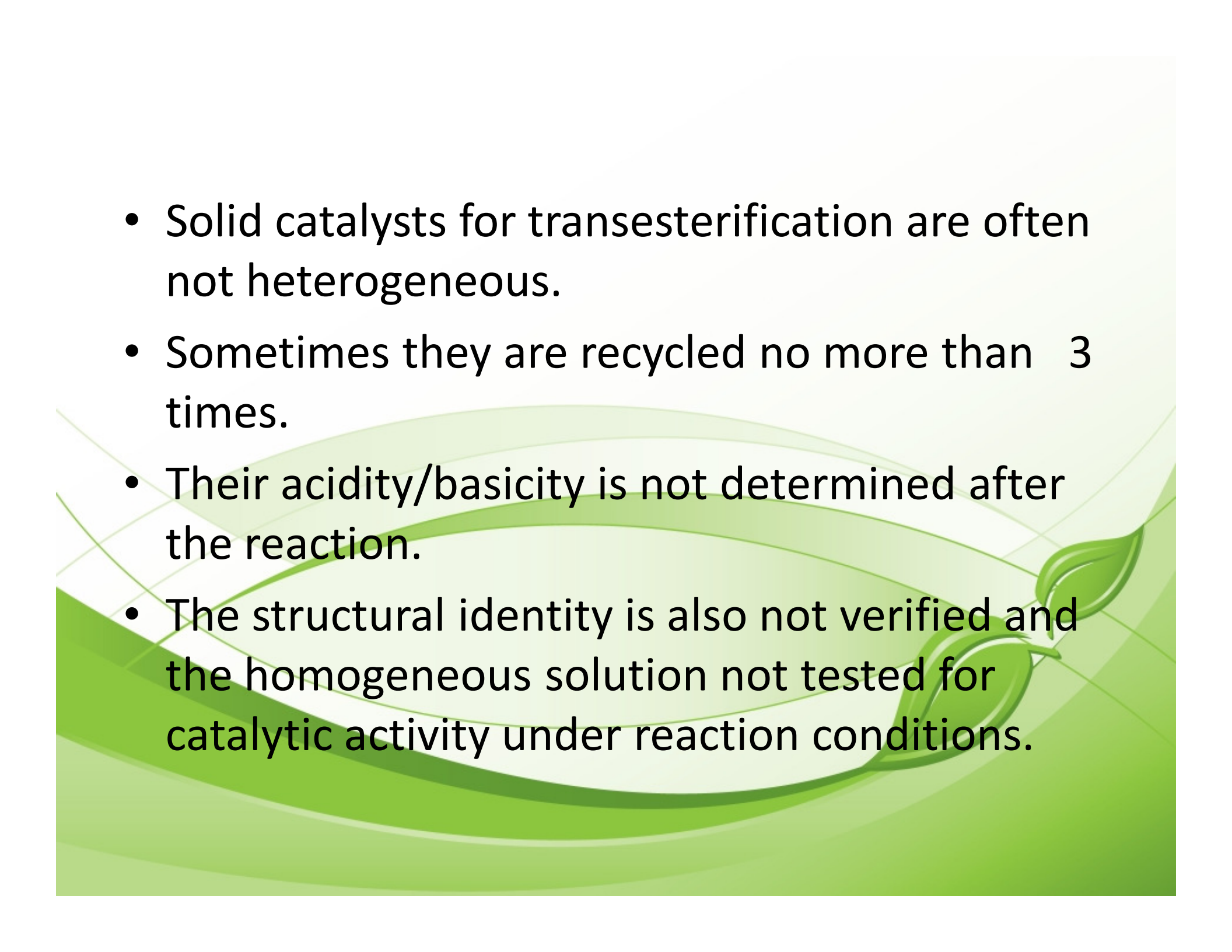
Heterogeneous acid catalysts, which promote simultaneously the alcoholysis of the triglycerides and the esterification of the free fatty acids, are, therefore, promising substitutes for homogeneous basic catalysts.

**Heterogeneous Catalysts for Liquid-Phase Oxidations:
Philosophers' Stones or Trojan Horses?**

ROGER A. SHELDON,^{*},[†] MARTIN WALLAU,[‡]
ISABEL W. C. E. ARENDS,[†] AND
ULF SCHUCHARDT^{*},[‡]

*Laboratory of Organic Chemistry and Catalysis,
Delft University of Technology, Julianalaan 136,
2628 BL Delft, The Netherlands, and Instituto de Química,
Universidade Estadual de Campinas, Campinas-SP, Brazil*

Acc. Chem. Res. **1998**, **31**, 485-493

- Solid catalysts for transesterification are often not heterogeneous.
 - Sometimes they are recycled no more than 3 times.
 - Their acidity/basicity is not determined after the reaction.
 - The structural identity is also not verified and the homogeneous solution not tested for catalytic activity under reaction conditions.
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Advantages of Solid Acid Catalysts

- Are tolerant to high contents of FFA: i.e. cooking oil can be used, but other cheap fats and oil cakes are also suitable,
- Are tolerant to higher water content : i.e. hydrated ethanol (95 %) can be used,
- Produce high quality Biodiesel: no washings are required if the catalyst does not leach,
- Give glycerol with high purity: easy workup and good value of the by-product.

Acid Zeolites

- Proton-exchanged Zeolites are very acidic and should be good catalysts. However, the pores are normally too small (exception MCM-41, etc).
- Zeolites are too hydrophilic.
- Proton-exchanged Mordenite affords FAME at high yields (95%). However, the presence of water dealuminates the zeolite and makes it less acidic.

Heteropolyacids

- HPA are slightly soluble in the reaction media: strong contribution of homogeneous catalysis is expected.
- This is also true for $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ and for supported HPA.
- The catalysts are promising for cooking oils with high content of FFA and H_2O .
- However, careful studies always show that these catalysts suffer from leaching. Thus, the contribution of homogeneous catalysis is not negligible.

Sulfated Zirconia

- Suitable acidity.
- High yields are achieved.
- Active in esterification and transesterification.
- The contribution of homogeneous catalysis can not be neglected. H_2SO_4 always leaches from the catalyst.
- Sulfated oxides also leach and are typically less active.
- Sulfated tin oxide and sulfated zirconia-alumina leach less and have improved lifetime.
- Deactivation is a common problem for all sulfonated catalysts.

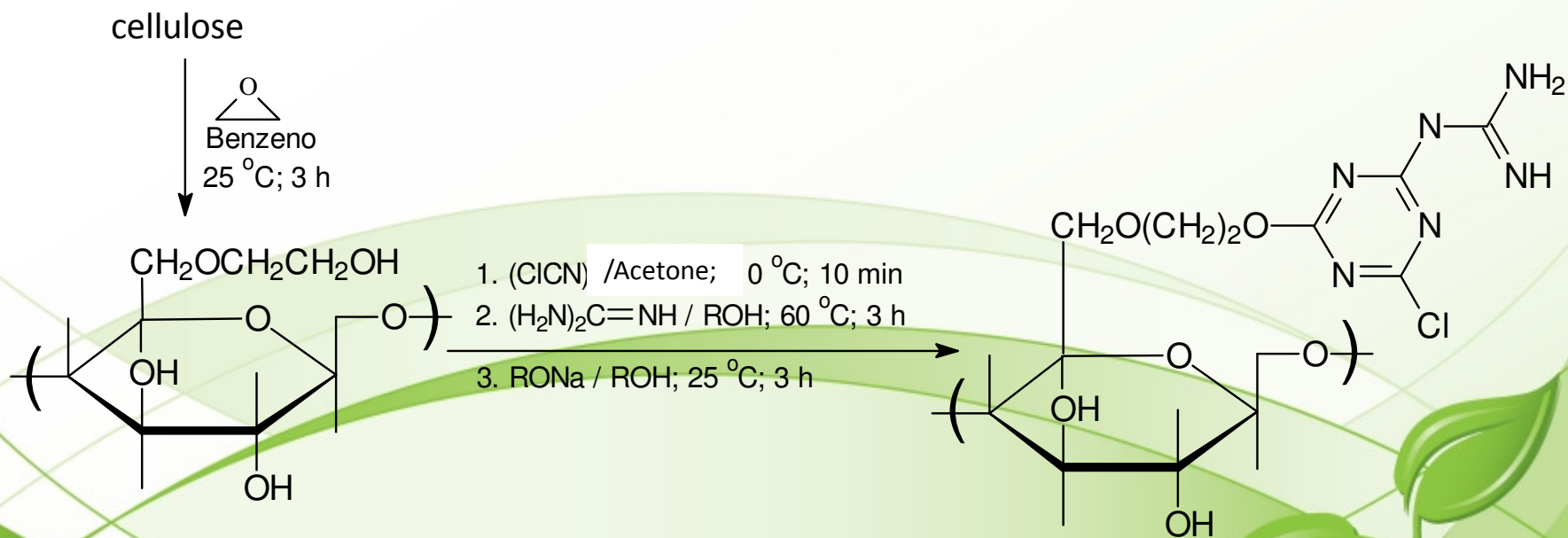
Ion-exchange Resins and Organic Supports

- Incomplete carbonization of carbohydrates, followed by sulfonation gives active catalysts.
- It is claimed that starch-derived catalysts can be recycled 50 times retaining 93 % of its catalytic activity, but there is no definite proof.
- Amberlyst 15 is active and can be recycled, however, its structure collapses after a larger number of cycles.
- Nafion does not show higher activity than Amberlyst 15.
- Sulfated PVA membranes are also very active but not enough stable.

Oxides and Double-Metal Cyanides

- Some oxides like ZnAl_2O_4 (Axens Technology) are Lewis acids and insoluble in the reaction medium, however, they are not very active and need drastic conditions (190°C, 2 h).
- $\text{ZnO-La}_2\text{O}_3$ also seems to be very promising.
- Fe-Zn double-metal cyanides (Ratmasamy et al.) are also Lewis acids and stable in the transesterification of vegetable oils and esterification of FFA.
- Reaction conditions are also drastic (170°C, 8 h), however, the catalyst seems to be totally stable.
- A fixed-bed continuous flow reactor was operated during 52 h, giving ~ 90% conversion.

The first totally heterogeneous basic catalyst and the first continuous process for transesterification was developed in our lab in the early 1980s.



Brazilian Patent BR 8202429

Basic Zeolites

- Alkali-ion-exchanged zeolites, Alkali-metal oxide clusters in zeolites, Cs-MCM-41, Cs-sepiolite, Mg-hydrotalcite are active, but quickly deactivate if FFA are present.
- Na or K mordenite, zeolite β and X are also active, however, the alkali metal leaches.
- Conversions for NaY are reported to be 95.1, 30.3 and 4.7 % after the 1st, 2nd and 3rd cycles.

Hydrotalcites

- Layered double hydroxides containing $\text{Mg}(\text{OH})_2$ with amorphous substitution of Mg^{2+} by Al^{3+} .
- Excess of positive charge compensated by anions such as OH^- .
- Calcination forms O^{2-} and O^- species.
- After each cycle, the catalyst should be calcinated to regenerate its activity.
- Suffer leaching, which results in MgO soaps.
- Are not suitable for the continuous process.

Basic Metal Oxides

- CaO acts as solid base catalyst; 1 h reflux gives 80 % yield of FAME. (MgO and Ba(OH)₂ are also active).
- However Ca(OMe)₂, Ca glyceroxides, Ca carboxylates, are formed acting as homogeneous catalysts.
- KF/ZnO and BaO/ZnO are also active but are partly dissolved in the reaction mixture.
- Ca(OMe)₂ displays good stability and excellent activity in transesterification and can be recycled 20 times. However, 4 % of catalyst were used and no report on catalyst losses/leaching is provided by the authors.
- Considerable contribution of homogeneous catalysis was found by other authors for the same catalyst.

Immobilized Metal Salts

- KI/Al₂O₃ (35 wt % KI) calcined at 773 K gives 96 % conversion; however, the catalyst is not very stable.
- The authors do not report recycling experiments.
- Na/NaOH-Al₂O₃ is very active but deactivates rapidly.
- K₂CO₃ or CaCO₃ are also active but dissolve slowly.
- CaO on SBA-15, MCM-41 or fumed silica show good interaction between CaO and support, reducing lixiviation, but only few cycles were reported.
- MgO impregnated on SBA-15 shows good activity (96 % conversion after 5 h), however, nothing is reported on catalyst deactivation.
- ZnO-La₂O₃ (Zn:La = 1:3) is only efficient at 200°C.

Solid organic Bases

- Guanidines heterogenized on polystyrenes are very active. We reported their use in up to 9 cycles. However, leaching is also observed.
- Encapsulated guanidines in zeolite Y and anchored to MCM-41 are not very efficient due to diffusion limitations.
- Salts of amino acids are also active.
- Zn arginate gives nearly 90 % yield at 135°C and 15 bar.

Enzymatic Catalysis

- Lipases effectively catalyze transesterification
- However, disadvantages are easy deactivation, low conversions, low rates and high costs.

Not topic of this talk

The background of the slide is a light green gradient with several overlapping, wavy, semi-transparent green bands that create a sense of movement. On the right side, there are three stylized green leaves with visible veins, arranged in a vertical line. The overall aesthetic is clean and modern, typical of a professional presentation.

Transesterification in Alternative Solvents

- In *supercritical methanol* (250°C, 8 MPa) no catalyst is required.
- Reaction is fast (few minutes), efficient (no diffusion problems), allowing 98 % yield.
- High-cost industrial plants.
- *Ionic liquids* facilitate separation of catalyst from reagents and products.
- However, activity losses due to leaching are also observed.
- Liberation of catalytic active species is detected.

Conclusions

- Solid Catalysts are environmentally friendly choices.
- Solid Catalysts are less active and suffer from deactivation.
- Massive research efforts are under way to develop materials with better acidic or basic properties.
- Solid Lewis Acids are very promising as shown by Axens Technology (Esterfip-H). Two esterfip-H plants in France and Sweden are in operation.

Conclusions

- The Mcgyan process uses fixed bed metal oxides ZrO_2/Al_2O_3 and supercritical methanol.
- Solid Brønsted acids will not be as good for commercialization as there is always leaching and deactivation involved.
- New solid base catalysts are very promising, especially at higher temperatures ($200^\circ C$) where FFA are also esterified and water is not anymore deactivating the catalyst.
- Enzyme technology is still far from commercial full-scale operation.

Design of solid catalysts for the conversion of biomass

Roberto Rinaldi and Ferdi Schüth*

The discovery and investigation of novel and efficient pathways for the conversion of biomass into biofuels and chemicals are among the big challenges facing heterogeneous catalysis nowadays. In this perspective article, we will address the key aspects that should be taken into account in the design of novel solid catalysts for the conversion of biomass.



Energy & Environmental Science, 2009, DOI: 10.1039/b902668a.