



Focus on CSIR research in Fine Chemicals

CSIR Biosciences

October 2006

A new process to produce fragrances from crude sulphated turpentine, a waste stream from the pulp and paper industry

Applying microreactor technology to a fine chemical process

Introduction

South Africa's pulp and paper industry currently produces 420 tons per annum of crude sulphated turpentine (CST) as a waste product of the Kraft sulphate wood pulping process. CST contains numerous sulphur compounds and as a result is foul-smelling and not environmentally friendly. The main components of CST are α -pinene (60-65%) and β -pinene (25-35%). This research project aims to develop a cost-effective process to produce citral (lemon odour), citronellol, and citronellal (used in soaps and detergents for a rosy, floral tone). Other intermediates produced are also valuable fragrance compounds and could be sold as such, e.g. pinanol, linalool, nerol, and geraniol.

Microreactor technology was also applied to some of the reaction steps as a more efficient and inexpensive alternative to conventional reactors to make the process more affordable for an SMME. A commercial partner, Clive Teubes cc, collaborated on the project, specifically on preparation of market samples for evaluation by potential customers.

Research Methodology

A laboratory process was developed as shown in the reaction scheme, Figure 1.

Laboratory experimental protocols were successfully developed for each reaction in the sequence. The process was also up-scaled to bench-scale where 100g samples of the various products were prepared. The process is currently at the pilot-plant scale and kilogram quantities of key intermediates and products will be produced as market samples for evaluation by potential customers. One of the key reactions, on which the success of the project hinges, is the pyrolysis of pinanol to linalool at 650 °C. Funding provided by the Technology and Human Resources for Industry Programme (THRIP), a programme managed by the National Research Foundation (NRF) on behalf of the Department of Trade and Industry (the dti), afforded the CSIR the

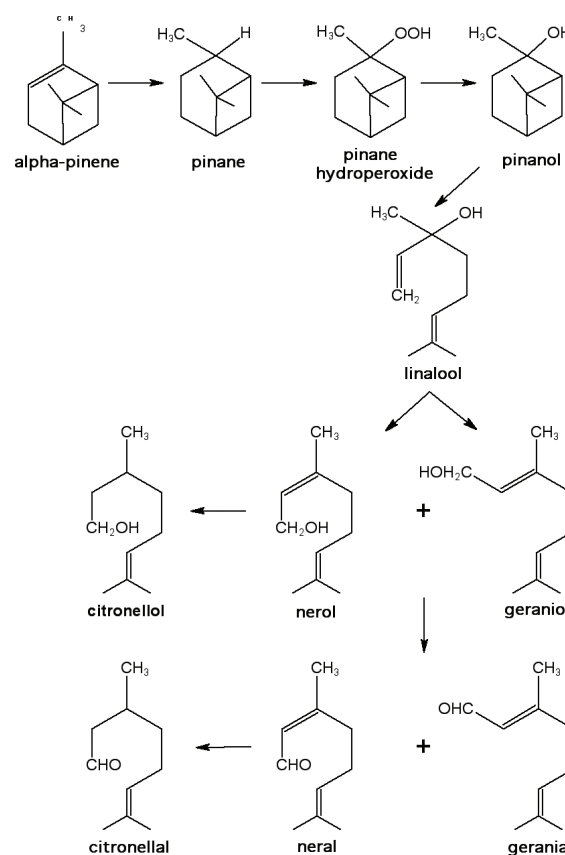


Figure 1: Scheme showing reaction sequence and products derived from CST

CSIR
our future through science



opportunity to design, purchase, and assemble the highly specialised equipment required to carry out this difficult reaction. This included microreactors, pulseless pumps, heating elements and temperature controllers. Micro-reactor technology was applied to several of the reactions to improve yields and make the process more affordable in terms of capital cost.

Results and Discussion

The results of the bench-scale experiments for each of the reaction steps in the sequence are summarised in Table 1, below:

of numerous by-products since the product itself can decompose under the reaction conditions.

The critical reaction in this process is the pyrolysis of pinanol which is thermally rearranged under gas phase conditions to linalool. These types of reactions are normally conducted in a flow-through tubular type reactor system. The residence time of the reactants (and product) in the reactor is relatively long because of the large diameter of the tube reactor (5-20mm). This is necessary to allow high conversions (>50%) of the substrate which is required for a commercial

mass and heat transfer coefficients (~55kW/m²) are significantly superior to a tubular reactor. As a result the reaction rate is extremely high and hence the residence time can be reduced to a few seconds. This results in lower rates of linalool decomposition and hence higher selectivities. Scale-up to production by replication of microreactors would eliminate costly design since only one engineering cycle would be needed.

Conclusions

A process was successfully developed up to bench-scale for the preparation of fragrance compounds from CST and 100g quantities of citral, citronellol and citronellal were produced. The advantages of using a microreactor as compared to a tubular reactor were demonstrated for the pyrolysis of pinanol to linalool.

Table 1: Results of Bench-scale experiments

Substrate	Product	Reaction Type	% Conversion	% Selectivity
α-Pinene	Pinane	Hydrogenation	95	90
Pinane	Pinane hydroperoxide	Oxidation	30	85
Pinane hydroperoxide	Pinanol	Reduction	90	98
Pinanol	Linalool	Pyrolysis (650 °C)	70	72
Linalool	Nerol/Geraniol	Isomerisation	80	98
Nerol/Geraniol	Neral/Geraniol (Citral)	Oxidation	100	98
Citral	Citronellol	Hydrogenation	89	86
Citral	Citronellal	Hydrogenation	97	86

In general, although these reactions have not been fully optimised, the conversions and selectivities to the required product have been very good. In the oxidation of pinane, the conversion has to be kept low in order to achieve higher selectivities. Higher conversions results in the formation

process. However, experiments have shown that at these high temperatures, linalool decomposition is significant and hence the selectivity is low (<50%). Reactions carried out in microreactors have significantly improved both the conversion (~70%) and selectivity (>70%).

The advantage of a microreaction system is that the channels in which the reaction occurs is very small (50-100µm) and the surface area to volume ratio is very high (9000-50 000m²/m³). Therefore, the



Contact details:
CSIR Biosciences

Subash Buddoo
Tel: (011) 605 2250
Email: sbuddoo@csir.co.za

www.csir.co.za