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Lappeenranta University of Technology

Satu Sundqvist

**REACTION KINETICS AND VISCOSITY MODELLING
IN THE FUSION SYNTHESSES OF Ca- AND Ca/Mg-RESINATES**

Acta Universitatis
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Lappeenranta University of Technology

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*Thesis for the degree of Doctor of Science (Technology) to
be presented with due permission for public examination
and criticism in the Auditorium of the Student Union House
at Lappeenranta University of Technology, Lappeenranta,
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Errata

<i>Page</i>	<i>Location</i>	<i>Correction</i>
13	first paragraph	... <u>ca.</u> 230 °C...
(I) 1680	last paragraph	viscosity unit is <u>mPa s</u>
(I) 1685	Eq. (9)	$r'_A = -\underline{2}k'c_A^2c_B$
(II) 469	Eq. (5)	
(I) 1686	Eq. (20)	<u>$c_A^{-1} - c_{A,0}^{-1} = k'''t$</u>

ABSTRACT

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Satu Sundqvist

Reaction kinetics and viscosity modelling in the fusion syntheses of Ca- and Ca/Mg-resinates

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Keywords: resinate, fusion method, printing ink, reaction kinetics, decarboxylation, FTIR, PLS

Rosin is a natural product from pine forests and it is used as a raw material in resinate syntheses. Resinates are polyvalent metal salts of rosin acids and especially Ca- and Ca/Mg- resinates find wide application in the printing ink industry. In this thesis, analytical methods were applied to increase general knowledge of resinate chemistry and the reaction kinetics was studied in order to model the non-linear solution viscosity increase during resinate syntheses by the fusion method.

Solution viscosity in toluene is an important quality factor for resinates to be used in printing inks. The concept of critical resinate concentration, c_{crit} , was introduced to define an abrupt change in viscosity dependence on resinate concentration in the solution. The concept was then used to explain the non-linear solution viscosity increase during resinate syntheses. A semi-empirical model with two estimated parameters was derived for the viscosity increase on the basis of apparent reaction kinetics. The model was used to control the viscosity and to predict the total reaction time of the resinate process.

The kinetic data from the complex reaction media was obtained by acid value titration and by FTIR spectroscopic analyses using a conventional calibration method to measure the resinate concentration and the concentration of free rosin acids. A multivariate calibration method was successfully applied to make partial least square (PLS) models for monitoring acid value and solution viscosity in both mid-infrared (MIR) and near-infrared (NIR) regions during the syntheses. The calibration models can be used for on-line resinate process monitoring.

In kinetic studies, two main reaction steps were observed during the syntheses. First a fast irreversible resination reaction occurs at 235 °C and then a slow thermal decarboxylation of rosin acids starts to take place at 265 °C. Rosin oil is formed during the decarboxylation reaction step causing significant mass loss as the rosin oil evaporates from the system while the viscosity increases to the target level. The mass balance of the syntheses was determined based on the resinate concentration increase during the decarboxylation reaction step.

A mechanistic study of the decarboxylation reaction was based on the observation that resinate molecules are partly solvated by rosin acids during the syntheses. Different decarboxylation mechanisms were proposed for the free and solvating rosin acids. The deduced kinetic model supported the analytical data of the syntheses in a wide resinate concentration region, over a wide range of viscosity values and at different reaction temperatures. In addition, the application of the kinetic model to the modified resinate syntheses gave a good fit.

A novel synthesis method with the addition of decarboxylated rosin (i.e. rosin oil) to the reaction mixture was introduced. The conversion of rosin acid to resinate was increased to the level necessary to obtain the target viscosity for the product at 235 °C. Due to a lower reaction temperature than in traditional fusion synthesis at 265 °C, thermal decarboxylation is avoided. As a consequence, the mass yield of the resinate syntheses can be increased from ca. 70% to almost 100% by recycling the added rosin oil.

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Lohja, November 1999

Satu Sundqvist

CONTENTS

LIST OF PUBLICATIONS	iii
NOMENCLATURE.....	iv
1 INTRODUCTION	1
2 AIMS OF THE STUDY	4
3 ROSIN BASED PRINTING INKS.....	5
3.1 Sources of rosin	5
3.2 Composition of rosin	5
3.3 Properties and use of rosin.....	6
3.4 Modified rosins in ink technology	7
3.4.1 Introduction to ink technology.....	7
3.4.2 Rosin modifications	7
4 SYNTHESIS METHODS AND USE OF RESINATES	9
4.1 Synthesis methods	9
4.1.1 Precipitation method.....	9
4.1.2 Solvent method.....	9
4.1.3 Fusion method	10
4.2 Use of resinsates.....	10
4.2.1 Resinsates in printing inks	10
4.2.2 Other uses of resinsates	11
5 RESINATE SYNTHESSES BY FUSION METHOD.....	12
5.1 Reaction steps	12
5.1.1 Resination reaction	13
5.1.2 Decarboxylation reaction.....	13
5.1.3 Side reactions.....	14
5.2 Modified syntheses	14
6 SUMMARY OF THE RESULTS	15
6.1 Critical resinate concentration	15
6.2 Improved analytical methods using FTIR spectroscopy	17
6.2.1 Conventional calibration method.....	17
6.2.2 Multivariate PLS calibration method	17

6.3	Reaction kinetics and modelling of syntheses	18
6.3.1	Main reaction steps	18
6.3.2	Empirical viscosity model	18
6.3.3	Resination reaction and mass balance of the system	19
6.3.4	Mechanistic model for decarboxylation reaction.....	20
6.3.5	Decarboxylation in a thermobalance	21
6.4	Modified resinate syntheses.....	22
6.4.1	Fortified syntheses	22
6.4.2	Application of the viscosity model in practical systems.....	24
6.4.3	Syntheses with rosin oil additions	26
7	CONCLUSIONS.....	27
	REFERENCES.....	29
	APPENDICES	
	Scientific publications I-V	

LIST OF PUBLICATIONS

The thesis is based on the following five scientific publications. In the text these publications will be referred to by their roman numerals (I-V).

- I Sundqvist, S., Paatero, E., Klemola, A., Tenhola, H., Solution Viscosity Increase in Fusion Synthesis of Ca/Mg-resinates, *AIChE Journal*, 44 (1998) 1680 - 1688.
- II Sundqvist, S., Paatero, E., Tenhola, H., Resination and Decarboxylation Reactions in Fusion Synthesis of Ca-resinates, *The Canadian Journal of Chemical Engineering*, 77 (1999) 465 - 472.
- III Sundqvist, S., Leppämäki, M., Paatero, E., Minkkinen, P., Application of IR Spectroscopy and Multivariate Calibration to Monitor the Fusion Synthesis of Ca- and Ca/Mg-resinates, *Analytica Chimica Acta*, 391 (1999) 269 - 276.
- IV Sundqvist, S., Turunen, S., Paatero, E., Decarboxylation of Rosin Acids in Fusion Synthesis of Ca-resinates — Thermogravimetric Studies, submitted 1999.
- V Sundqvist, S., Turunen, S., Paatero, E., Twigt, F., Modified Syntheses of Ca-resinates by Fusion Method, submitted 1999.

NOMENCLATURE

Symbols

a = parameter in Eqs (6.7) and (6.8), $(\text{Pa s})^{-1}$

b = parameter in Eqs (6.7) and (6.8), $(\text{Pa s}^2)^{-1}$

c_i = concentration of compound i , mol/kg

c_1 = resinate concentration at time t_1 , mol/kg

c_2 = resinate concentration at time t_2 , mol/kg

$c_{\text{RCOOH(s)}}$ = concentration of solvating rosin acids, mol/kg

$c_{\text{RCOOH(f)}}$ = concentration of free rosin acids, mol/kg

c_{crit} = critical resinate concentration, w-%

c_x = concentration of ion pairs, Eq. (6.14), mol/kg

k'' = rate constant for the decarboxylation reaction, $(\text{mol/kg})^{-0.5} \text{ min}^{-1}$

k_1 = rate constant for the decarboxylation of solvating rosin acids, $(\text{mol/kg}) \text{ min}^{-1}$

k_2 = rate constant for the decarboxylation of free rosin acids, $(\text{mol/kg})^{-1} \text{ min}^{-1}$

K_{ass} = equilibrium constant for the protolysis of free rosin acids, -

K'_{ass} = equilibrium constant for the protolysis of fortified rosin acids, -

m_1 = mass of the reaction mixture at time t_1 , kg

m_2 = mass of the reaction mixture at time t_2 , kg

n_i = amount of i in the reactor, mol

r_i = generation rate of compound i , $(\text{mol/kg})^{1-\alpha} \text{ min}^{-1}$

t_{50} = critical reaction time, min

α = reaction order, -

η = viscosity, Pa s

Δm_{rel} = relative mass loss, -

Abbreviations

AV = acid value

EVA = polyethenevinylacetate co-polymer

FA = fumaric acid

FTIR = Fourier transform infrared-spectroscopy

MAA = maleic acid anhydride

MIR = mid-infrared region

NIR = near-infrared region

PFR = phenolformaldehyde resin

PLS = partial least square regression

R^{\cdot} = carbanion intermediate

Definitions

acid (number) value, AV

titrated acid concentration in units of [mg(KOH)/g(sample)],
corresponding to the acid concentration in units of [mol/kg] as:

$$c_{\text{COOH}} = \frac{AV}{M_{\text{KOH}}} = \frac{AV}{56.11 \text{ g/mol}}$$

fortification

rosin is reacted with FA or MAA to get fortified rosin, which is used as a raw material for syntheses of fortified resins with improved printing qualities

liming

rosin is reacted with Ca(OH)_2 to get Ca-resinate

resinate

metal salts of rosin acids

rosin acids

abietic and pimaric type resin acids in rosin

rosin oil

i.e. decarboxylated rosin,

neutral component formed in the decarboxylation reaction step

vehicle

resin/solvent combinations used in printing inks

1 INTRODUCTION

Tall oil rosin is obtained as a by-product of sulphate pulping of pine trees. Other types of rosins are obtained by tapping pine trees (gum rosin) or by extraction from virgin pine stumps (wood rosin). All three types of rosin consist of about 90% rosin acids, 2% fatty acids and 8% neutral components. Resinates are polyvalent metal salts of rosin acids, such as calcium, magnesium and zinc salts (Figure 1.1). In the syntheses of Ca- and Ca/Mg-resinates, calcium and magnesium hydroxide and calcium acetate are mainly used as the reactive metal salts. The resinates find wide application as dryers for paints and varnishes and as constituents of printing inks.

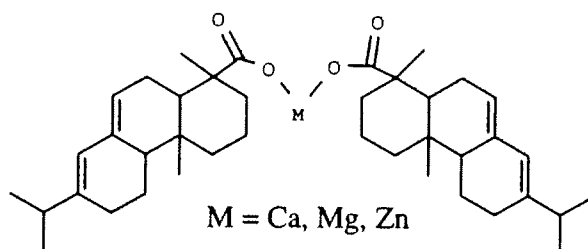


Figure 1.1 — Resinate molecule scheme.

Resinates are produced from rosin by three different methods: fusion, solution and precipitation method. The most important industrial methods are the solution method and the fusion method. In industrial applications, however, pure calcium resinates synthesised from monomeric rosin are known to crystallise or otherwise solidify (block) during the reaction, especially at higher metal levels. High metal contents are often needed to give sufficiently high viscosity to the resinate solution. The target value for the solution viscosity of the resinate varies depending on the application. In the present study the target value for the solution viscosity of the resinates is in the range of 50 - 100 mPa s at 50 w-% resinate-toluene solutions. A concentration of 50 w-% resinate in solution is generally used as reference concentration in printing ink industry.

A difficulty during the fusion resinate synthesis, in addition to the blocking phenomena, is an abrupt change in the physical properties of the resinate, especially in solution viscosity. During the synthesis the increase in solution viscosity at a given resinate concentration turns almost exponential at a specific reaction time. In addition, especially in a large-scale industrial fusion resinate process, there are batch-to-batch variations in reaction times for obtaining the target viscosity. These variations can only partly be explained by a non-homogenous raw material, i.e. rosin, used in the process. No kinetic model has been proposed

for the non-linear viscosity increase for batches of different characteristics in viscosity behaviour during fusion syntheses. Therefore, it has been difficult to control a resinate process and to obtain a product with the desired solution viscosity. Due to the lack of detailed knowledge of the phenomena on a molecular level, the chemical factors affecting the macroscopic properties of the reaction mixture (especially viscosity) have remained unexplained.

The viscosity problems related to the blocking phenomenon have been observed by some authors (Petrone, 1971, Panda & Panda, 1985), but no explanation of the cause of this kind of behaviour has previously been published. In this thesis (I) the reason for the abrupt viscosity increase with increasing resinate concentration in the solution is explained by resinate molecular interactions and excluded volume effects, and the concept of critical resinate concentration, c_{crit} , is introduced. The definition of the critical resinate concentration is applied to explain the non-linear viscosity increase of 50 w-% resinate–toluene solution during syntheses. In addition, in I a semi-empirical model for the solution viscosity increase during the syntheses is developed on the basis of acid value titration data. The two-parameter viscosity model is currently being used to control the progress of an industrial fusion resinate process.

In the synthesis of Ca-resinates simple kinetic measurements are generally based on acid value determinations, conventionally by off-line titration with KOH. The titration gives the overall state of the system: the progress of the resination reaction and the decarboxylation of rosin acids. An industrial scale fusion resinate process is usually followed by solution viscosity measurements of reaction media. However, the measurement of 50 w-% resinate–toluene solution viscosity, which is an important quality factor for resins to be used as an ink vehicle, is time consuming, and the acid value titration does not give enough information about the reaction system. A new method for determining the composition of the complex reaction mixture (resinate concentration and free rosin acid concentration) by FTIR using conventional calibration method is introduced in II.

In fusion synthesis the reaction steps include a fast irreversible resination reaction and a slow decarboxylation reaction of rosin acids forming neutral rosin oil. In addition, side reactions, isomerisation and polymerisation (mainly thermal dimerisation) of rosin acids, take place. The isomerisation and polymerisation mechanisms of rosin acids have been studied by Sinclair *et al.*, 1970 and Zinkel, 1983. However, in this study these side reactions have minor importance, because the isomerisation does not have a direct effect on viscosity and the polymerisation occurs only to a very small extent. In fortified resinate syntheses, rosin is first fortified by reacting with a dienophile, such as maleic acid or its anhydride, or fumaric acid. The reaction products are tricarboxylic acids, which are referred to as maleopimaric or

fumaropimaric acids. The rosin adducts have a high melting point and their high acidity makes them reactive with metal hydroxides to form resinates with improved printing qualities.

The main reaction steps in fusion syntheses, resination reaction and thermal decarboxylation of rosin acids, have not been studied to the same extent as the side reactions. The resination reaction cannot occur to a target level due to the blocking of the unreacted $\text{Ca}(\text{OH})_2$ and problems in increased melt viscosity (Petrone, 1971; Jilek, 1976; Panda & Panda, 1985). Therefore, the viscosity is often raised to the desired level by increasing the resinate concentration in the reactor indirectly by raising the temperature to enable the decarboxylation reaction to take place. In the decarboxylation reaction step rosin oil is formed and evaporated from the system. Thus the decarboxylation reaction is an essential reaction step, although it has the negative consequence that it lowers the mass yield. Furthermore, the decarboxylation reaction increases the total reaction time of the resinate process. The kinetics and mechanisms of the main reaction steps of resinate syntheses are studied in **II**.

In the development of a kinetic model for resinate syntheses, the concentrations of the chemical species of the reaction mixture are needed, especially at the initial stages of the reactions and at frequent intervals. It is also important to monitor and control the solution viscosity during an industrial scale resinate process. A near-infrared (NIR) spectrometer with an optical fibre probe can be used in-line, and is, therefore, ideal for both the kinetic and process control applications, if the calibration problems typical for this technique can be solved. In **III** partial least squares (PLS) regression is successfully applied to the calibration of multiwavelength spectra of the complex resinate reaction mixture. The advantage of this method is that all the wavelengths can be included in the calibration. In the mid-infrared region this treatment of data is also more informative than recording only one or two wavelengths of the spectrum.

The kinetic model of decarboxylation is extended in **IV** to cover a wider resinate concentration region to obtain resinates in a wider viscosity region than in the reference synthesis used in the derivation of the kinetic model. In addition, in **IV** the application of thermogravimetric measurements to demonstrate the decarboxylation reaction during the resinate synthesis is studied. The effects of different reaction temperatures and atmospheres on the decarboxylation reaction are studied in a thermobalance.

The mechanistic model for the decarboxylation of rosin acids and PLS calibration models are applied to modified resinate syntheses in **V**. Modifications are made by using different amounts of fumaric acid and maleic acid anhydride in fortifying the rosin. In addition, a new modification of fusion resinate synthesis based on rosin oil addition is introduced.

2 AIMS OF THE STUDY

In the field of resinate chemistry, little academic research has been carried out in the 90's and only a few scientific publications have been published in recent years. The aim of this thesis is to increase general knowledge of resinate chemistry in order to understand and model the viscosity behaviour of the resins during syntheses. Kinetic and reaction mechanistic studies are based on the increased understanding of chemical and physical interactions of molecules in the resinate reaction mixture.

In the kinetic studies of the syntheses, the aim was first to develop analytical methods to obtain kinetic data. Tools for process control were then developed based on the analytical data and the reaction kinetics. However, the aim in this thesis was not to model an industrial reactor and, therefore, factors like mixing and distillation of rosin oil were not studied.

The application of FTIR analyses to measure the composition of the resinate reaction mixture was introduced. In addition, improved analytical methods were applied to avoid analytical and sampling problems of the complex reaction mixture. The application of a multivariate calibration method with FTIR analyses was introduced in mid-infrared (MIR) and near-infrared (NIR) regions. The kinetics of decarboxylation was studied in a thermobalance for easier monitoring of the reaction at different temperatures and in different atmospheres.

In the study of modified resinate syntheses, the aim was to find out the effect of the amount of fortifying substances, fumaric acid and maleic acid anhydride, on the reaction kinetics. In addition, a new modification of fusion synthesis was developed with the aim of avoiding the decarboxylation reaction step, which causes a significant mass loss in the syntheses. In the novel syntheses introduced in this study, the viscosity of the resinate is adjusted with the increased conversion of Ca(OH)_2 to resinate obtained by the addition of rosin oil during the syntheses.

3 ROSIN BASED PRINTING INKS

3.1 Sources of rosin

Pine forests are the primary source of rosin, classified as gum, wood and tall oil rosin. Gum rosin is obtained by distillation of volatile turpentine from oleoresin exuded from a wound in living pine trees. Wood rosin is obtained by solvent extraction of pine stump wood along with the removal of the turpentine by steam distillation. Tall oil rosin is obtained by recovering and fractionating the crude tall oil in the pulp industry. In the alkaline soda and kraft pulping processes, the rosin and fatty acids in the wood are solubilised by the hot spent liquor, from which they are separated as crude tall oil (Kirk and Otmer, 1969).

For hundreds of years, only gum rosin was produced commercially. Wood rosin, since its preparation in 1910, gradually gained prominence and eventually its production exceeded that of gum rosin. Tall oil was not used as a major source of rosin until the mid 1950's. Since that time, however, it has become an extremely valuable rosin source and it is now the major contributor in the manufacture of synthetic resins. In future, more and more tall oil rosin will be used, because with modern distilling technology purer rosin can be obtained. There is also the possibility of further improvements to the quality of tall oil-based resins and improvements in quality uniformity (Petrone, 1971; Alalauri and Luttinen, 1989).

3.2 Composition of rosin

The principal component of rosin are rosin acids, which are monocarboxylic acids of alkyl hydro-phenanthrene. Rosin acids occur in pine in a number of isomeric forms which have the molecular formula $C_{20}H_{30}O_2$ (Figure 3.1). Sixteen rosin acids have been identified in Finnish tall oil rosin by gas chromatography-mass spectrometry (GC-MS). In addition to the rosin content, there is a small proportion of fatty acids, unsaponifiable material and a very small quantity of sulphur-containing compounds in tall oil rosin (Oldring and Hayward, 1987; Chen, 1992).

The distribution of the rosin acid isomers found in pine trees varies depending on their geographic location and, perhaps equally important, on the thermal history of the rosin. It has been shown that rosin acid composition between crude tall oil and tall oil rosin changes substantially during the high temperature fractionation process. One of the most obvious changes is a large decrease in abietic acid (from ca. 54% to 36%) and a corresponding increase in the more stable dehydroabietic acid (from ca. 18% to 33%). Furthermore, some of the rosin acids originally not present in crude tall oil are found after distillation. This is mainly due to decomposition, dehydrogenation, isomerisation and disproportionation reactions which take place during fractionation (Hon and Shiraishi, 1991; Chen, 1992).

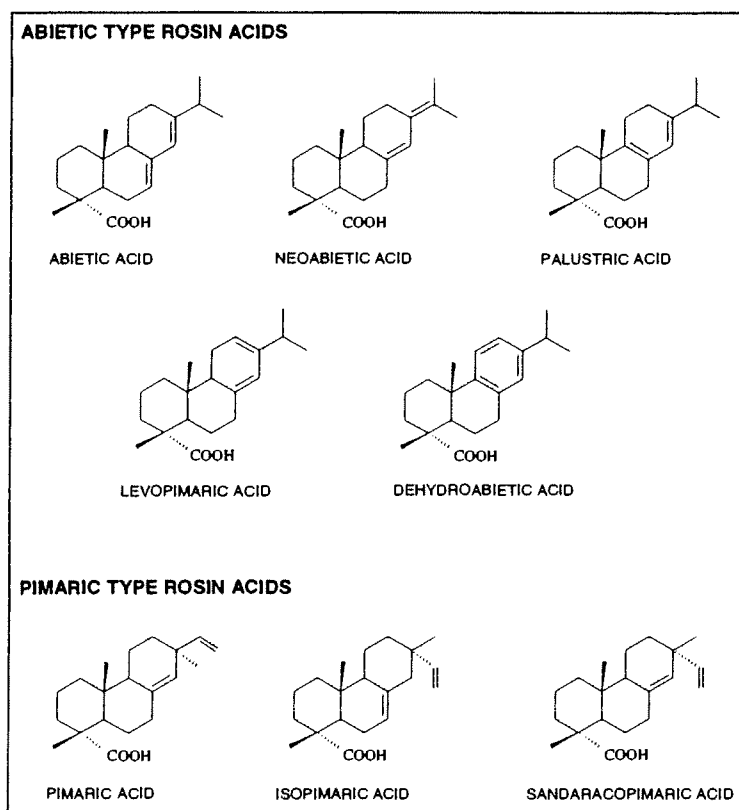


Figure 3.1 — Abietic and pimaric type rosin acid isomers.

3.3 Properties and use of rosin

Rosin varies considerably in colour, from a very pale yellow through dark red to almost black, depending on the source and method of processing. It is generally translucent, brittle at room temperature, and has a slight turpentine odour. It is readily soluble in most organic solvents, but insoluble in water. Rosin is graded by colour and tested for foreign matter, softening point, acid value and saponification number (Kirk and Otmer, 1969).

Rosin as obtained from its three major sources is called unmodified rosin. Unmodified rosins have a tendency to crystallise and oxidise. Crystallisation can be reduced by heating, polymerisation, partial neutralisation with sodium hydroxide, or via reactions with dienophiles. Oxidation can be reduced by disproportionation, hydrogenation and to some extent by polymerisation. Chemical treatment, such as polymerisation, increases the stability and improves the physical properties of rosin through modification of the phenanthrene-derived moiety and such chemically treated products are called modified rosin (Kirk and Otmer, 1969; Oldring and Hayward, 1987).

The chemical reactions of rosins, based on abietic acid structure, give the most important properties of the rosin. The carboxyl group enables conversions to esters and salts, while the double bonds are reactive sites for maleic and fumaric adducts, and, for example, polymerisation reactions. The molecular structure of rosin acids accounts for organic solubility and water insolubility.

The most important use of pure rosin has been in paper size production, but nowadays rosin derivatives are widely used in adhesives, surface coatings, polymerisation emulsifiers and in printing inks. Because of its high acidity pure rosin has limited use in the printing ink industry, such as in cheap quality inks. The acidity is responsible for feeding with basic pigments. The rosin film extends to leave a residual tack on application to a thin film. Rosin is, however, used extensively in the printing ink industry in its modified forms, such as resinates (Panda & Panda, 1985).

3.4 Modified rosins in ink technology

3.4.1 Introduction to ink technology

The ink industry is one of the most important markets for rosin based products. An ink is a specific type of coating consisting of a colorant dispersed in a resin/solvent combination. The type of the solvent used depends on the printing method and use for the ink.

There is an infinite number of resin/solvent combinations (called vehicles) which can be used to make printing inks. Proper selection is important since the vehicle controls viscosity, flow, evaporation rates of the carrier solvent, press stability, toxicity, odour and, of course, printability. The resin/solvent combination must have the ability to properly wet the colorant and the printing substrate.

Nearly all types of printing inks may be made from rosin because rosin based derivatives provide a broad range of solubility and compatibility with film formers and other commonly used ink modifiers. This characteristic distinguishes rosin-derived materials from other available natural and synthetic resins. This is important since rosin derivatives are rarely used alone in printing inks. Most often they are used in conjunction with other resins, alkyds and higher molecular weight (polymeric) film formers (Zinkel and Russel, 1989).

3.4.2 Rosin modifications

The rosin acid molecule possesses two chemically reactive centres, the double bonds and the carboxyl group. These reactive centres enable many modifications in structure and numerous derivatives to be obtained. Because rosin is composed of a number of different isomers of rosin acids, the chemistry of its reactions, which yields rosins useful in printing ink production, is relatively complex (Kirk and Otmer, 1969).

Oxides, hydroxides, salts and various metal compounds react with the carboxyl group to form soaps and resinsates. Alkali metals form simple water soluble rosin salts that are used in pigment resination. Rosin salts of alkaline earth metals (Ca, Mg, Zn) are soluble in organic solvents and have good pigment wetting. They are widely used in letterpress and publication gravure inks and vehicles (Zinkel and Russel, 1989).

Many rosin esters are available commercially and are used in a variety of applications. Rosins are most commonly combined with polyhydric alcohols, i.e. alcohols with more than one hydroxyl group. The glycerol ester (ester gum) was the first ester used for protective coatings. The low acidity of estergum permits its use in ink containing basic pigments, such as zinc oxide, which is impossible with unmodified rosin. Estergum shows resistance to hydrolysis, emulsification and pigment livering. It has found use in heat set letter press aluminium octoate gels, as resinsates retard gelation of the aluminium. Estergum is, however, too slow in the release for gravure. The introduction of pentaerythritol esters in the 1930s resulted in two greatly improved properties for varnishes. The products were harder and more durable. The pentaerythritol esters have softening points about 15 °C higher than those of analogous glycerol esters (Petrone, 1971; Panda & Panda, 1985; Zinkel and Russel, 1989).

In printing inks, the most important double bond reaction of rosin is with dibasic acids such as fumaric acid or maleic acid anhydride. These react via a Diels-Alder addition mechanism to form tribasic acids. The rosin adducts have high melting points and they are used for quick set inks, rotogravure inks and heat set media. Combined with resinsates in heat set letter press ink, these resins exhibit good rub resistance (Panda & Panda, 1985).

In addition, oxidation can occur at the double bond sites causing the rosin to darken, become brittle and less soluble in aliphatic solvents. As a result, for use in many chemical and physical processes, the rosin must be stabilised by hydrogenation, disproportionation and polymerisation. Only the polymerisation of rosin is significant in inks and vehicles.

4 SYNTHESIS METHODS AND USE OF RESINATES

4.1 Synthesis methods

Rosin acids, being acidic, readily undergo reaction with bases, such as calcium or magnesium hydroxide, calcium acetate and zinc oxide, forming metal resinates. Three different methods are used for resinate formation: precipitation method, solvent method and fusion method. Industrial applications are generally based on the solvent or the fusion method. In Finland, resinates have been produced by the fusion method since 1987 in Valkeakoski plant, which is nowadays a part of International Paper Company's unit, Arizona Chemical. In this thesis the resinates were synthesised by the fusion method and industrial samples from fusion resinate process were used in large-scale applications.

4.1.1 *Precipitation method*

A water soluble metal salt, for example $\text{Ca}(\text{OH})_2$, is added to an aqueous solution of the sodium salt of rosin. This precipitates the resinate, which is then filtered, washed and dried. The precipitated resinate is a light tan powder having a calcium content near six per cent. The product has little or no free rosin acids present, so the melting point is higher than that of the fused resinate. The solubility of the precipitated compound in organic solvents is much less than that of the fused product, which is only partially neutralised (Jilek, 1976; Oldring and Hayward, 1987).

4.1.2 *Solvent method*

The rosin is dissolved in a hydrocarbon solvent and heated with a reactive metal compound. The materials react at the boiling point of the solvent. Reactive metal compounds include oxides, hydroxides, acetates and carbonates. When the reaction is complete, solvent and other volatile materials are removed. Care must be taken to ensure complete reaction, otherwise there will be a suspension of the metal compound which will give rise to haziness in the resinate (Jilek, 1976; Oldring and Hayward, 1987).

The resination reaction can be carried out at room temperature if a solution of rosin is added to a suspension of $\text{Ca}(\text{OH})_2$. This inverse-addition-order method introduced by Jilek, 1976, enables the production of resinate with lower manufacturing costs. However, difficulties have been observed in obtaining target viscosities without blocking of the unreacted $\text{Ca}(\text{OH})_2$.

4.1.3 *Fusion method*

The chemistry of the fusion method is similar to that of the solvent method. A reactive metal compound is added to molten rosin at ca. 230 - 300 °C. The amount of rosin converted to resinate is less than when using the other methods due to the thermal decarboxylation of rosin acids at high temperatures. Acid values below 40 mg(KOH)/g are seldom formed because of dispersion problems with Ca(OH)_2 . Over-reaction leads to the formation of an infusible gel. A combined Zn/Ca-resinate has a much lower acid value and higher melting point than when calcium alone is used (Jilek, 1976; Oldring and Hayward, 1987). The fusion method is studied in this thesis and will be described more in detail in Section 5.

4.2 Use of resinsates

4.2.1 *Resinsates in printing inks*

To be used as an ink vehicle a solution of Ca-resinsates should have a viscosity of ca. 500 mPa s, at about 50 w-% resinate concentration. Solids much above 50 - 55 w-% result in too high costs for the finished product. Furthermore, the resinsates must be homogenous, free of suspended matter and crystals, and soluble in the particular solvent (Jilek, 1976).

Both Ca- and Ca/Zn-resinsates find wide application in roto press supplement, magazine and coated paper work. In high speed presses, resinsates with a very high melting point and fast release properties are necessary. On the other hand, the necessity of very high melting point (170 - 180 °C) resinsates presents certain problems because these resinsates are highly limed (6 - 7% of rosin). If the resin is not filtered, certain pigments will react with free Ca(OH)_2 in ball mill processing, resulting in gelation and colour burn out (Panda & Panda, 1985).

Zinc resinsates and zinc-calcium resinsates, though they are more expensive than calcium resinsates, have gained in commercial importance. Zn/Ca-resinsates have better stability and higher melting points usually at lower viscosities than calcium resinsates. They are less reactive, almost inert, with basic pigments and wet many pigments better than limed rosins. To reduce costs and to improve the physico-chemical characteristics of Zn- and Ca-resinsates, other resinsates (like magnesium resinsates) are also synthesised and used for printing purposes (Panda & Panda, 1985).

Because resinate films are rather powdery and they give poor rub resistance and tend to penetrate paper substrates, they are commonly used with a polymeric film former. Resinsates are compatible with numerous film formers. Both ethyl- and ethyl-hydroxyethylcellulose (EHEC) modify resinsates for improved rub and abrasion resistance and reduced tack in the gravure process (Zinkel and Russel, 1989).

5 RESINATE SYNTHESIS BY FUSION METHOD

5.1 Reaction steps

In fusion resinate synthesis, two reaction steps can be observed in an inert atmosphere (Figure 5.1). A fast resination reaction takes place at ca. 235 °C. Then the temperature is increased to the final reaction temperature (above 260 °C) and a thermal decarboxylation of rosin acids starts to take place. The resinate concentration in the reactor increases during the decarboxylation step due to evaporation of neutral rosin oil, which is formed during the decarboxylation reaction. The increased resinate concentration and the decreased rosin acid concentration result in the desired composition for the reaction mixture. As a consequence, the target solution viscosity (> 50 mPa s) for fusion resinsates to be used as binders in printing ink industry is obtained.

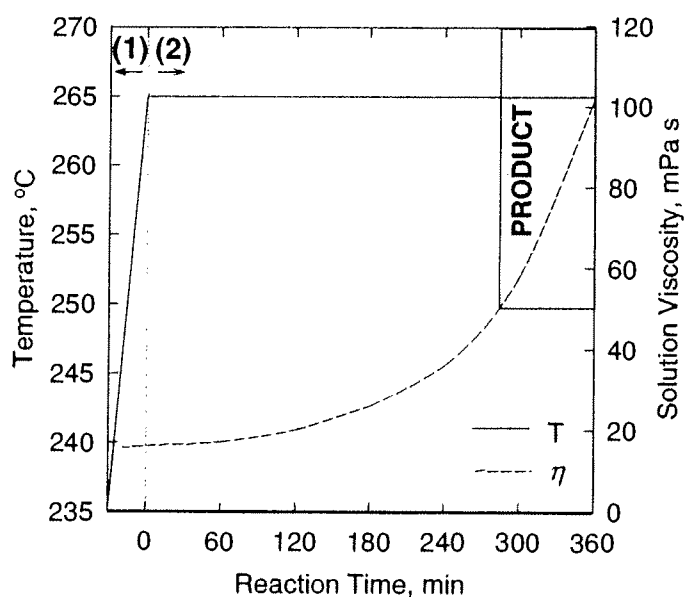


Figure 5.1 — Temperature and viscosity profiles in resinate synthesis. Target viscosity for the product is 50 mPa s for 50 w-% resinate–toluene solution.

(1) Resination reaction: $2 \text{RCOOH} + \text{Ca(OH)}_2 \longrightarrow (\text{RCOO})_2\text{Ca} + 2 \text{H}_2\text{O}\uparrow$

(2) Thermal decarboxylation reaction: $\text{RCOOH} \longrightarrow \text{RH}\uparrow + \text{CO}_2\uparrow$

4.2.2 *Other uses of resins*

The potassium, sodium, ammonium and amine salts of rosin are used as emulsifiers. Ca- and Zn-resins are soluble in mineral spirits and are used, in addition to in printing inks, as a gloss oil in paints and varnishes. Heavy metal soaps of rosin acids can function as driers for paints and varnishes. Metallic resins also find use in ceramic colours, pyrotechnics, tile adhesives and generally where a harder and less acidic thermoplastic resin than rosin is required (Kirk and Othmer, 1969; Oldring and Hayward, 1987).

5.1.1 Resination reaction

In fusion synthesis, a fast and irreversible resination reaction takes place at temperatures above 230 °C, as reactive metal salts, for example calcium hydroxide, magnesium hydroxide and calcium acetate, are added to the molten rosin. A nitrogen atmosphere is used to apply an inert atmosphere in order to avoid side reactions, such as oxidative decarboxylation. The conversions of the metal salts to resinate varies from 75% to 95% depending on the degree of neutralisation of the rosin and the purity of the metal salt. Due to the incomplete resination reaction, traces of unreacted metal salts are observed in the product.

The resination reaction is a fast reaction step in fusion resinate syntheses and studies on the reaction kinetics have not previously been published. Separate studies on resination and decarboxylation reaction steps have been difficult to carry out due to the lack of an analytical method for quantitative measurement of resinate concentration during the fusion resinate syntheses.

5.1.2 Decarboxylation reaction

The reaction temperature of fusion synthesis is increased to 265 - 285 °C after the resination reaction is considered to be complete. In that temperature range, the thermal decarboxylation of rosin acids takes place forming neutral rosin oil. Consequently, the acid value and melting point of the reaction mixture decreases. The rosin oil evaporates from the system causing the increased resinate concentration in the reaction mixture. When a target viscosity for the product is obtained, the mass yield of the synthesis is only ca. 70%.

Decarboxylation of rosin acids is either a thermal or an oxidative reaction. Rosin acid decarboxylation has been studied at different temperatures (300 - 360 °C), by Wideman and Kuczkowski (1985), and in different atmospheres, by Szogalski and Mitskevich (1983, 1987). In fusion resinate syntheses, oxidative decarboxylation is avoided by using an inert atmosphere (nitrogen). The rate of thermal decarboxylation depends on temperature: the reaction is faster at high temperatures. If rosin oil formation is desired, decarboxylation can be promoted, according to Oldring and Hayward, 1987, by using catalysts like zinc, chloride and sulphuric acid at temperatures of 150 - 270 °C. Rosin oil finds limited use in the ink and paint industries.

The oxidative and thermal decarboxylation reactions are very important and need to be considered in the manufacturing and storing of resinates. Studies on degrees of decarboxylation of rosin acids during resinate syntheses have not previously been published. This is probably due to that evaporated rosin oil is not easy to collect and to weigh quantitatively. As a consequence, it has been difficult to define the mass balance of fusion syntheses.

5.1.3 Side reactions

In this study, side reactions during the resinate syntheses have minor importance. The polymerisation reaction of rosin acids has been observed to be mainly thermal dimerisation in nitrogen atmosphere, and the dimerisation takes place only to a very small extent during resinate syntheses (Sundqvist, 1994). The isomerisation reaction of rosin acids plays an important role in rosin acid fortification with fumaric acid and maleic acid anhydride. However, the isomerisation reaction can be neglected when studying the main reaction steps in fusion resinate syntheses, i.e. the resination reaction and decarboxylation of rosin acids and modified rosin.

5.2 Modified syntheses

Rosin modified with maleic acid anhydride (MAA) or fumaric acid (FA) is extensively used as a raw material in fortified resinate syntheses. The Diels-Alder type of addition is possible with levopimaric acid but not with abietic acid as the reaction does not take place when conjugation is in two rings. As the temperature is increased, abietic acid isomerises to levopimaric acid and the addition reaction takes place. The adduct has a high melting point and a high acid content, and it is soluble in alcohols and glycols. The high acidity makes it reactive with metal hydroxides to form resinates. Fumaric acid (FA) possesses a structure which, due to its steric hindrance, leads to slower reactions and different characteristics than maleic. The reduced reactivity of FA with rosin is evident from the fact that the reaction is not as exothermic as the reaction of rosin with MAA (Panda & Panda, 1985).

In fortified resinate syntheses the rosin is first fortified by adding fumaric acid or maleic acid anhydride into the rosin melt at 195 °C. The reaction time is two hours. Then the temperature is increased to 235 °C and the reactive metal salts are added into the reaction mixture. After the resination reaction is complete, the temperature is increased to the final reaction temperature (265 - 285 °C) and the thermal decarboxylation takes place causing the rosin oil to evaporate, and the target viscosity for the fortified resinate to be reached.

6 SUMMARY OF THE RESULTS

6.1 Critical resinate concentration

Non-linear viscosity increase causes difficulties in controlling fusion resinate syntheses and in obtaining a product with the desired target viscosity value. In order to understand the non-linear viscosity increase of resinate–toluene solutions during the syntheses, solution viscosity of resins was measured at different weight fractions in toluene. The viscosity of Ca/Mg-resins was observed to be highly dependent on the weight fraction of the resinate in the solution (Figure 6.1). The increase in viscosity turned almost exponential after a specific concentration value. This concentration value was determined based on a *log log* plot of viscosity and concentration data (I, Fig. 2) and denoted as the critical resinate concentration, c_{crit} . The change in viscosity dependence on resinate concentration implies a transition from a dilute solution to a concentrated region, where molecular interactions have a stronger influence on viscosity.

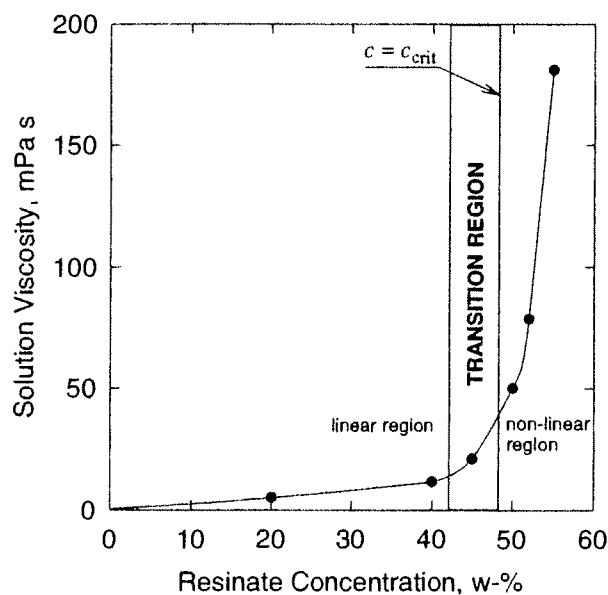


Figure 6.1 — Viscosity behaviour of the resinate ($c_{crit} = 48.1$ w-%) in toluene solution.

In the critical concentration region molecular interactions were studied using a FTIR spectroscopy, a vapour pressure osmometer and a density analyser. The density measurements revealed that a relative mixing parameter of resinate–toluene solutions is independent of resinate concentration at low concentrations. However, an increase in the mixing parameter value was observed above 20 w-% resinate concentration (I, Fig. 3). The increase reflects a transition towards more dense packing of the molecules in the mixture. Based on these results, it was concluded that there are three concentration regions in the viscosity behaviour of the resins (Figure 6.1): a linear region, where the resinate concentration is much smaller than the critical value ($c \ll c_{\text{crit}}$), a transition region near the critical concentration value, and a non-linear viscosity increase region ($c > c_{\text{crit}}$), where the molecules form a sufficiently dense packing for increased molecular interactions.

In fusion syntheses, while monitoring the viscosity of 50 w-% resinate–toluene solution, the viscosity increase is observed to change at a specific reaction time, denoted by t_{50} (Figure 6.2). At this reaction time, the resinate reaction mixture has reached the chemical composition (i.e. concentration ratio of rosin acid to resinate) corresponding to the critical value, $c_{\text{crit}} = 50$ w-%. After the reaction time t_{50} , the high viscosity values of 50 w-% resinate–toluene solutions are based on the increased molecular interactions in toluene. Calculation of the time t_{50} is done according to Equation (6.8) introduced in Section 6.3.

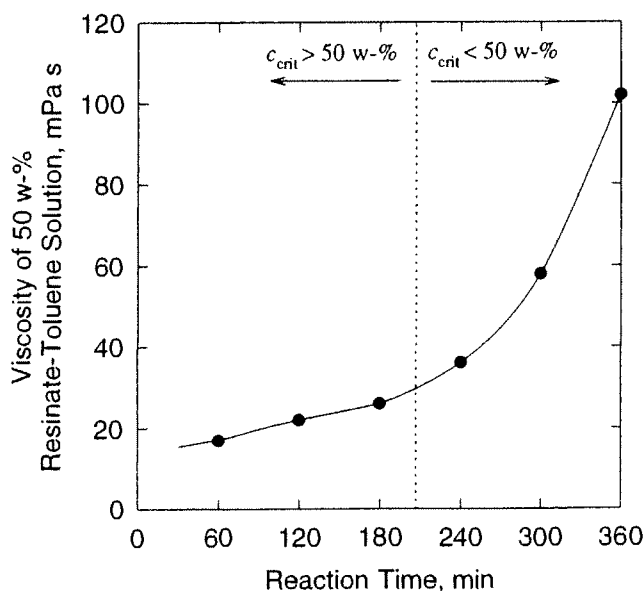


Figure 6.2 — Solution viscosity increase in fusion resinate synthesis. The reaction time t_{50} is denoted with a dotted line ($t_{50} = 207$ min).

6.2 Improved analytical methods using FTIR spectroscopy

The kinetic studies require that the composition of the complex resinate reaction mixture can be analysed. In earlier studies of resinates, only the acid value has been monitored during the syntheses (Sundqvist, 1994). In this study FTIR spectroscopy has been utilised by applying a conventional calibration method and a multivariate calibration method to obtain more information of the progress of the syntheses.

6.2.1 Conventional calibration method

Pure abietic acid was used as a standard for rosin consisting of abietic type rosin acids (about 85%) and pimaric type acids (about 15%). These isomers differ only in the location of their two double bonds. Ca-abietate was synthesised by the inverse-addition-order method (introduced by Jilek, 1976) and it was used as a standard for Ca-resinate. The formation of Ca-abietate occurred at room temperature and the yield of pure Ca-abietate was 97%. Acid value titration of the Ca-abietate indicated that no decarboxylation reaction had occurred.

The relative FTIR absorbance of the mixture of Ca-abietate and abietic acids in the 15 w-% toluene solution (II, Fig. 2) showed a linear relationship in the concentration region studied. Therefore, this method is applicable for determining the resinate concentration and the concentration of the free rosin acids (capable of associating to dimers in toluene) of the reaction mixture.

Solvation phenomenon. When FTIR results were compared to acid value titration data, it was observed that all the acids titrated are not free to associate to dimers in 15 w-% toluene solution analysed by FTIR. This was explained by a solvation phenomenon in the resinate reaction mixture. In a fusion state resinate process, the solvent molecules (rosin acids) may become linked to the dissolved resinate molecules, as a result of the interaction between these molecules. Thus the resinate molecules are partly solvated by the rosin acids in the fusion state resinate process.

6.2.2 Multivariate PLS calibration method

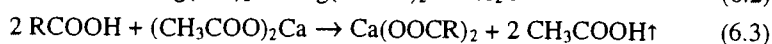
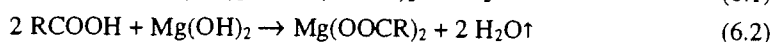
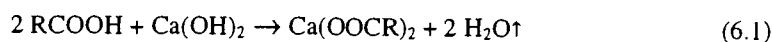
Conventionally calibrated FTIR measurement is an appropriate method for analysing the composition of the resinate reaction mixture. However, this method requires sample pre-treatment, as the resinate is dissolved into toluene (15 w-% solution). Furthermore, the sampling is not easy to carry out during the fusion state resinate process. Due to the relatively high reaction temperature (265 °C), the application of direct in-line viscosity monitoring is technically difficult. Therefore, in this thesis an indirect monitoring system for resinate syntheses was studied. Multivariate calibration models from the FTIR data of the syntheses were derived to enable on-line sampling and monitoring the solution viscosity as well as the reaction kinetics during the resinate process.

Mid-infrared region (MIR) and near-infrared region (NIR) were used separately in the calibrations of acid value and viscosity data by a multivariate calibration method. Predictive calibration models based on partial least squares (PLS) regression were developed to describe the relationship between the spectra and acid value or viscosity data. It was observed that pre-processing of the spectra with multiplicative scatter correction was necessary before the calibrations, and the results showed that the models in the MIR and NIR regions were equally good for calibration purposes. In acid value calibrations linear PLS was sufficient for calibrations, even when different rosin grades were used in the syntheses (III, Figs 4, 6 and 7). But for solution viscosity calibrations, non-linear PLS had to be applied to obtain satisfactory calibration models (III, Figs 5 and 8).

6.3 Reaction kinetics and modelling of syntheses

6.3.1 Main reaction steps

Reactions of the acid groups during the resinate synthesis are resinate formation (6.1)-(6.3) and decarboxylation (6.4).



By assuming that water and acetic acid are completely removed from the reaction mixture due to the relatively high reaction temperature ($T > 230^\circ\text{C}$) the rate laws (6.5) and (6.6) are written for the irreversible resination and decarboxylation reactions, respectively:

$$r'_A = -2k'c_A^2c_B \quad (6.5)$$

$$r''_A = -k''c_A \quad (6.6)$$

where A denotes a carboxylic acid group and B is Ca(OH)_2 , Mg(OH)_2 or $(\text{CH}_3\text{COO})_2\text{Ca}$.

6.3.2 Empirical viscosity model

Kinetic studies were first carried out by a conventional method using acid value titration, which gives the result of the overall state of the system: the progress of the resination reaction and the decarboxylation of rosin acids.

Based on the derived reaction rate equations (17) and (18) in I, the total reaction order for rosin acid decarboxylation is between one and two. Since the final aim was to obtain a viscosity model, it was sufficient to include the kinetic model in a simplified form. The simplified model was best illustrated with the second order rate equation.

The empirical correlation between the viscosity of 50 w-% resinate–toluene solution and the acid concentration in the reaction vessel was derived from the analytical data. The final viscosity model was obtained by combining the second order rate equation and the empirical correlation between acid value and viscosity data. The simplified form of the derived viscosity model is:

$$\frac{1}{\eta} = a + b t \quad (6.7)$$

This two parameter model provides a good description for the viscosity of the resinate solution as a function of reaction time (I, Fig. 11). Parameter a describes the viscosity level at the reaction time $t = 0$ (the smaller the value of a , the higher the initial value of the viscosity). Parameter b includes the rate constant from the kinetic model thus illustrating the rate of the viscosity increase.

By applying the model to process control, the viscosity increase of the resinate solution and the total reaction time of the batch can be estimated. The reaction time at which the viscosity increase changes is denoted by t_{50} . This critical time can be predicted according to the following equation derived in I:

$$t_{50} = -\frac{1}{2} \frac{a}{b} \quad (6.8)$$

This equation includes the parameters a and b , which are the same as in the viscosity model, Equation (6.7).

6.3.3 Resination reaction and mass balance of the system

The resination reaction was observed to be a fast irreversible reaction at a temperature range of 190 - 235 °C. The reaction was complete in about 15 minutes, and at 235 °C the conversion of $\text{Ca}(\text{OH})_2$ was 97%. The thermal decarboxylation reaction was regarded as insignificant in this temperature range in a nitrogen atmosphere, as the acid value remained constant after the resination reaction was complete (II, Fig. 5).

During the resination reaction, the concentration ratio of solvating to free rosin acids changes depending on the reaction temperature (II, Fig. 6). The fraction of the solvating acids increases with the increased resinate concentration, indicating that the resinate molecules are partly solvated by the rosin acids.

In fusion synthesis, the decarboxylation reaction of rosin acids takes place after the resination reaction is complete at 235 °C and the temperature is increased to the final reaction temperature (265 °C). Due to the vaporisation of the neutral rosin oil from the reaction system, the resinate concentration increases. In the experimental setup, the neutral rosin oil could not be collected and weighed quantitatively because it either solidified blocking the distillation column or escaped from the system.

The mass loss during the decarboxylation reaction for six hours was measured as about 30 w-%. The mass balance was calculated by regarding the resinate amount as remaining constant. The increase in the resinate concentration indicates the relative mass loss of the system, and the loss can be calculated according to Equation (6.9) derived in II from the mass balance equation:

$$\Delta m_{rel} = 1 - m_2/m_1 = 1 - c_1/c_2 \quad (6.9)$$

where c_1 and c_2 denote the resinate concentrations in mol/kg, and m_1 and m_2 denote the masses of the reaction mixture at the reaction times t_1 and t_2 , respectively.

6.3.4 Mechanistic model for decarboxylation reaction

The deduced mechanism for the rosin acid decarboxylation in the reaction mixture was based on the different reaction steps of the solvating and free rosin acids analysed by FTIR.

For the free rosin acids, the protolysis equilibrium of the ion pair formation was considered. By applying the quasi-equilibrium approximation, Eq. (11) in II, for the ion pair formation and considering that the solvating rosin acids decarboxylate straight according to first order kinetics, with respect to the rosin acid, the total decarboxylation rate of rosin acids became:

$$r_{deca} = k_1 c_{RCOOH(s)} + k_2 K_{ass} c_{RCOOH(f)}^2 \quad (6.10)$$

where k_1 and k_2 denote the decarboxylation rate constants for the solvating forms of rosin acids, $RCOOH(s)$, and for the free acids, $RCOOH(f)$, respectively. K_{ass} is the equilibrium constant of the ion pair association.

The reaction rate parameters were estimated separately according to the partial reaction rate equations (6.11) for the solvating and the free rosin acids ($i = \text{RCOOH(s)}, \text{RCOOH(f)}$). The overall rate equation (6.12) for decarboxylation was presented by means of partial reaction kinetics.

$$r_i = -\frac{1}{m} \frac{dn_i}{dt} = k_i c_i^{\alpha_i} \quad (6.11)$$

$$r_{\text{tot}} = r_{\text{RCOOH(s)}} + r_{\text{RCOOH(f)}} \quad (6.12)$$

If $r_{\text{RCOOH(s)}}$ and $r_{\text{RCOOH(f)}}$ are considered as being equal, the total reaction order for rosin acids is adjusted to $\alpha_{\text{tot}} = 1.5$.

The kinetic parameters were estimated from the differential equation (6.11) using the Simflex algorithm (Spendley, 1962). The differential equations were solved by means of linear multistep methods implemented in ODESSA, which is based on the LSODE software (Hindmarsh, 1983). The methods are available in the MODEST software (Haario, 1994). The kinetic model, Equations (6.11) and (6.12), supported well the deduced reaction mechanism (II, Fig. 7).

The kinetic model for the decarboxylation was verified with three demonstrating syntheses at different temperatures (265 - 285 °C). The Arrhenius parameters for the total decarboxylation of rosin acids were calculated based on the syntheses. The apparent activation energy for the thermal decarboxylation in Ca-resinate syntheses was observed to be 27 kJ/mol. The decarboxylation reaction of rosin acids was seen to take place in a very narrow temperature range: at 235 °C no decarboxylation was observed in 60 minutes and temperatures higher than 265 °C gave only a small rise to the decarboxylation reaction rate and amount.

6.3.5 Decarboxylation in a thermobalance

In the resinate syntheses, the mass loss is due to the evaporation of neutral rosin oil and carbon dioxide, which are formed during the decarboxylation reaction. The decarboxylation reaction of rosin acids during the resinate syntheses was demonstrated in a thermobalance. The study showed that the results of the decarboxylation kinetics obtained in the synthesis reactor compare favourably with thermogravimetric (TG) measurements (IV, Fig. 2). TG studies were applied to avoid the difficult sampling procedure of the complex reaction mixture. The effect of temperature and different atmospheres on the decarboxylation reaction were studied in a thermobalance.

Effect of atmosphere. TG measurements were carried out in nitrogen, carbon dioxide and air atmospheres at 260 °C in order to compare the thermal and the oxidative decarboxylation reaction of rosin acids in the resinate reaction mixture. It was observed that in the CO₂-atmosphere the decarboxylation followed the thermal decarboxylation curve of the reaction in the N₂-atmosphere. In the air atmosphere, the oxidative decarboxylation of the rosin was observed to be faster than the thermal decarboxylation during the first two hours (IV, Fig. 3). After that, however, the oxidative decarboxylation was restricted by the apparent reaction equilibrium.

Effect of temperature. The kinetic study of the thermal decarboxylation reaction was carried out in a thermobalance in a nitrogen atmosphere at different temperatures between 245 - 275 °C. The results of the syntheses with different target acid values, i. e. different amounts of Ca(OH)₂, followed well the change in total acid amount estimated by the kinetic model (IV, Fig. 5). In addition, it was observed that the distillation rate of rosin oil is proportional to the decarboxylation reaction rate and thus the distillation rate can be considered as being lumped into the kinetic model of decarboxylation.

6.4 Modified resinate syntheses

Rosin used as a raw material in resinate syntheses was fortified using fumaric acid (FA) or maleic acid anhydride (MAA) in order to get resinsates with improved printing qualities. Other modifications were done by using polymerised rosin as a raw material in fusion synthesis, or adding macromolecules to the reaction mixture in order to adjust the viscosity of resinate-toluene solutions to a higher level (> 100 mPa s) than in the unmodified syntheses. Polyethenevinylacetate co-polymer (EVA) was used as a non-reactive macromolecule and phenolformaldehyde resin (PFR) as a reactive modification substance. Fortifying substances, fumaric acid and maleic acid anhydride, were used in the EVA modified syntheses.

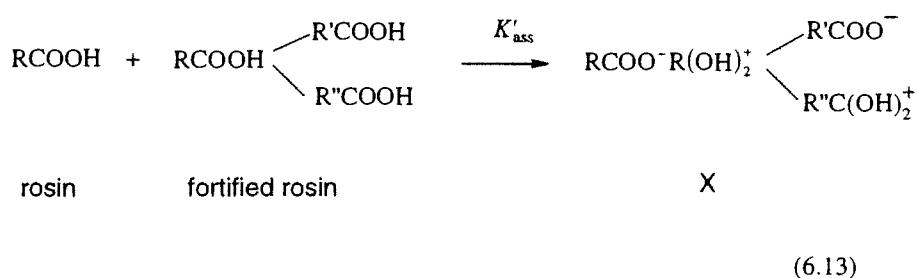
A new modification based on rosin oil addition before the resination reaction step was studied as a way of increasing the mass yield of resinate syntheses.

6.4.1 Fortified syntheses

The effect of the additions of fortifying substances (FA or MAA) on the decarboxylation reaction mechanism was studied based on the ratio of the free and solvating rosin acids in the reaction mixture. In addition, a multivariate calibration model applying PLS-regression was developed using FTIR data in order to monitor the acid value decrease and viscosity increase of the reaction mixture during the resinate syntheses.

Mechanistic model for decarboxylation. The deduced mechanism for the unfortified rosin acid decarboxylation in the reaction mixture is based on the different reaction steps of solvating and the free rosin acids analysed by FTIR. In the fortified resinate syntheses, it was observed that the fortified rosin acid groups are free to associate to dimers in toluene solution analysed by FTIR (V, Fig. 5).

In the case of fortified rosin acids, there are three acid groups. Therefore, the assumed equilibrium for the free acids becomes:



The quasi-equilibrium approximation is applied to this rapid step (6.13) to express the concentration of the ion pairs X:

$$c_X = K'_{\text{ass}} c_{\text{RCOOH}}^4 \quad (6.14)$$

By taking into account Equation (6.14) and assuming that the solvating rosin acids decarboxylate according to first order kinetics, with respect to the rosin acid, the total decarboxylation rate of fortified rosin acids becomes:

$$r_{\text{deca}} = k_1 c_{\text{RCOOH(s)}} + k_2 K'_{\text{ass}} c_{\text{RCOOH(f)}}^4 \quad (6.15)$$

where k_1 and k_2 denote the decarboxylation rate constants for the solvating forms of rosin acids, RCOOH(s) , and for the free acids, RCOOH(f) , respectively. K'_{ass} is the equilibrium constant of the ion pair association of fortified rosin.

It was observed that the kinetic model with the deduced reaction mechanism is well fitted to the analytical data (V, Fig. 6). The reaction order for total rosin acid decarboxylation varies from 1.5 to 2.5 depending on the amount of fortifying substance used.

PLS calibration model. In the fortified resinate syntheses, multivariate calibration models based on a linear PLS regression were applied to monitor the acid concentration decrease on the basis of FTIR spectroscopic data in the mid-infrared region. Randomised calibration data, using fortifying substances 2 - 6 w-% of the rosin amount in the syntheses, gave useful models for monitoring purposes (V, Fig. 8).

When the non-linear PLS was applied to calibrate the 50 w-% toluene solution viscosity of fortified industrial Ca/Mg-resinate samples, satisfactory calibration models were obtained in both the mid-infrared and near-infrared regions (III, Figs 5 and 8). However, NIR technique offers more options for process instrumentation due to the easier application of fibre optic probes.

6.4.2 Application of the viscosity model in practical systems

Practical resinate manufacturing processes are generally carried out by using fortified rosin as a raw material. Different modification substances can also be used in order to obtain resinsates with high viscosity values and improved printing qualities.

The empirical viscosity model, Equation (6.7), is used for monitoring fortified Ca/Mg-resinate processes. The independent parameters a and b are calculated based on viscosity samples at two different reaction times in the beginning of the resinate process. The estimated parameter values are then used for the prediction of the solution viscosity increase during the process. A total reaction time of the batch needed to obtain a target solution viscosity value for the product can also be estimated by the viscosity model.

An industrial Ca/Mg-resinate process using fortified rosin as the raw material follows well the empirical viscosity model (Figure 6.3) with the estimated parameter values a and b as shown in Table I. The viscosity values in seconds (measured using a standardised method with a DIN-4 cup) have been changed to the corresponding values in mPa s units. The data was obtained from the resinate process using off-line viscosity monitoring. This explains the small number of observations, which is not optimal for statistical interpretation of the fit of the viscosity model.

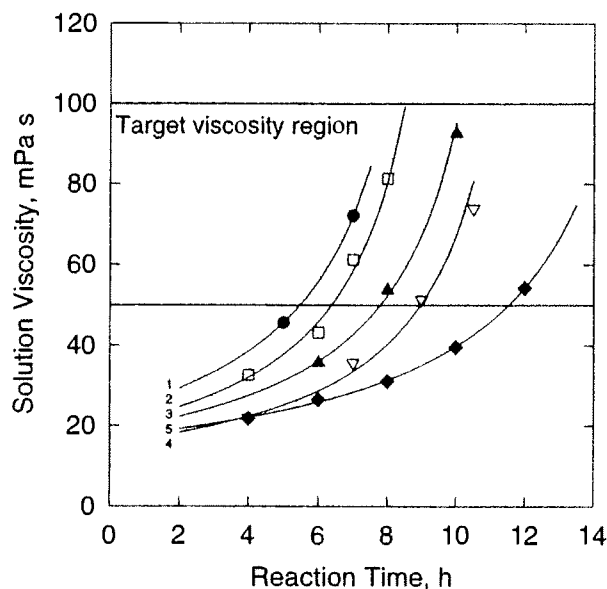


Figure 6.3 — Viscosity increase of the 50 w-% resinate-toluene solutions during the fusion resinate process. The samples are from different batches of an industrial Ca/Mg-resinate process. The lines are calculated according to the viscosity model, Eq. (6.7).

Table I — Estimated parameter values for the viscosity model, Eq. (6.7), of process data and the correlation coefficients of the fit.

Batch number	$ a $ (mPa s) ⁻¹	$ b $ (mPa s) ⁻¹ s ⁻¹	Number of data points	Correlation coefficient
1	0.0421	0.00403	2	-
2	0.0499	0.00469	4	0.985
3	0.0536	0.00430	3	0.997
4	0.0647	0.00499	4	0.990
5	0.0588	0.00337	5	0.998

The empirical viscosity model, Equation (6.7), was also applied to the modified syntheses in order to increase the solution viscosity in resinate process to a higher level ($\eta > 100$ mPa s). It was observed that the resinate syntheses from fortified rosin as well as those of slightly modified (EVA or PFR) rosin are well fitted to the empirical viscosity model (I, Fig. 11). It is obvious that severe modifications change the viscosity increase in the resinate synthesis because factors other than resination reaction and decarboxylation also affect viscosity. In the synthesis using polymerised rosin, the high viscosity values are partly due to the rosin dimers

present in the reaction mixture. PFR can react with rosin acids and hence increase the viscosity. EVA addition changes the ratio of viscosity to acid concentration because of the higher viscosity level caused by the macromolecules being added to the reaction mixture.

6.4.3 *Syntheses with rosin oil additions*

A new modification of the fusion synthesis with the addition of decarboxylated rosin (rosin oil) was introduced. The rosin oil addition enables higher degree of neutralisation of rosin acids in the resination reaction step than in traditional fusion syntheses. Therefore the target viscosity for the resinate can be obtained without the decarboxylation reaction step.

Rosin oil modified resinate syntheses were carried out at 235 °C. Because of the lower reaction temperature, thermal decarboxylation is avoided. The addition of rosin oil (20 - 40 w-% of rosin amount) to the reaction mixture enabled further resination reaction with a higher neutralisation degree of the rosin acids. Due to the higher resinate concentration in the reaction mixture, the solution viscosity of the resinate increases to the desired level when the rosin oil is evaporated. The mass yield of the rosin oil modified syntheses is as high as 100% because of the possibility of recycling the added rosin oil back into the reaction mixture.

7 CONCLUSIONS

This study showed that the fusion Ca- and Ca/Mg-resinate syntheses in the laboratory and in the industrial scale can be controlled by the semi-empirical viscosity model derived for 50 w-% resinate–toluene solution. The non-linear solution viscosity increase after the critical reaction time, t_{50} , is explained by the increased molecular interactions and excluded volume effects in the reaction mixture as the chemical composition, corresponding to the critical resinate concentration value $c_{\text{crit}} = 50$ w-%, is obtained in the syntheses.

The improved analytical methods were developed for the complex reaction media in order to study the reactions taking place in fusion resinate syntheses. FTIR analyses using a conventional calibration method in the mid-infrared region were applied to measure resinate concentration and free rosin acid concentration of the reaction mixture. It was observed, however, that all the rosin acids were not free to associate to dimers in toluene, and so they did not show any absorbance in FTIR. It was concluded that the resinate molecules are partly solvated by the rosin acid moiety due to the increased molecular interactions in fusion resinate syntheses.

In developing analytical methods for monitoring resinate syntheses, FTIR data was calibrated with a multivariate method applying partial least squares regression (PLS) in both the mid-infrared and near-infrared regions. The derived calibration models can be used in monitoring acid value and solution viscosity of fusion Ca-resinate syntheses and industrial Ca/Mg-resinate processes. By combining on-line sampling systems with the NIR technique, the sampling difficulties caused by the complex reaction media can be avoided.

The kinetic study revealed that there are two main reaction steps in fusion resinate syntheses. A fast irreversible resination reaction takes place at 235 °C, and it is followed by a slow thermal decarboxylation reaction of rosin acids at 265 °C. The study of the resination reaction enabled the mass balance calculation of the whole reaction system. Mechanistic study of the decarboxylation reaction was based on the different mechanisms of free and solvating rosin acids. The solvating rosin acids were observed to decarboxylate according to first order kinetics and the free rosin acids decarboxylated according to second order kinetics via a reaction equilibrium of the ion pair formation. The empirical data fitted well to the mechanistic model based on the differential rate equations of the decarboxylation reaction.

It was observed that the results of the decarboxylation kinetics obtained in the synthesis reactor compare favourably with thermogravimetric (TG) measurements. Therefore TG could be used to avoid difficulties in sampling and in analytical treatment of the complex reaction media. The studies of decarboxylation in different atmospheres and at different temperatures

were carried out in a thermobalance. Based on the TG results, the thermal decarboxylation of rosin acids in inert nitrogen and carbon dioxide atmospheres is slower than the oxidative decarboxylation in an air atmosphere in the beginning of the reaction. However, after the oxidative decarboxylation is restricted by the equilibrium state of the reaction, the thermal decarboxylation still continues.

The kinetic model for thermal decarboxylation was derived using the calcium content corresponding to the theoretical target acid value 70 mg(KOH)/g in the reference synthesis. The model was extended to cover a wider viscosity range of the product using target acid values 50 - 90 mg(KOH)/g in the syntheses. The kinetic model was also applied to TG studies at different reaction temperatures resulting in an almost constant value of apparent activation energy in all the syntheses with different target acid values. The value of the apparent activation energy includes the distillation rate of the rosin oil because the distillation rate was observed to be proportional to the decarboxylation reaction rate. Therefore the distillation rate can be considered as being lumped into the kinetic model. However, when modelling an industrial scale reactor the distillation and mixing in the reactor have to be taken into account to make the model complete.

Kinetics of fortified resinate syntheses using fumaric acid and maleic acid anhydride as fortifying substances was modelled with basically the same kind of mechanistic model as derived for unmodified resinate syntheses. The acid groups in the fortified rosin were observed to be free acid groups capable of associating to dimers in toluene. The free acid groups of fortified rosin decarboxylate via ion pair formation resulting in the apparent reaction order 4.0 for the free acids.

In addition, a new modification of resinate synthesis using rosin oil additions during the fusion synthesis is introduced. The rosin oil addition enables a higher degree of neutralisation of rosin acids in the resination reaction step than in traditional fusion syntheses. Thus the target viscosity for the resinate, to be used as a binder in printing ink industry, can be obtained without the decarboxylation reaction step. The possibility of avoiding rosin oil formation and recycling the added rosin oil considerably improves the mass yield of resinate syntheses.

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Solution Viscosity Increase in Fusion Synthesis of Ca/Mg-Resinates

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The effect of Ca/Mg-resinate concentration on solution viscosity was studied in toluene. The viscosity was observed to increase drastically above a specific concentration value. The change in viscosity dependence on concentration implies a transition from a dilute to a concentrated regime, where viscous dissipation is governed by resinate molecular interactions and excluded volume effects. The concept of critical resinate concentration, c_{crit} , was applied and used to explain the nonlinear solution-viscosity increase during the resinate synthesis. Ca/Mg-resinates were synthesized by the fusion method at 265°C in a laboratory-scale batch reactor. During the syntheses the increase in 50 wt. % toluene solution viscosity of the resinate turned almost exponential at a specific reaction time, denoted by t_{50} . Based on the apparent reaction kinetics, a semiempirical model with two estimated parameters was derived for the solution viscosity to be used for the prediction of the t_{50} time of resinate syntheses.

Introduction

Resinates are the rosin salts of polyvalent metals, such as calcium, zinc, and manganese (Figure 1). These kinds of resinates find wide application as dryers for paints and varnishes and as constituents of printing inks.

Resinates are produced by three different methods: fusion, solution, and the precipitation method. In order to improve the printing qualities of the resinate, rosin is generally first fortified by reacting with a dienophile, such as maleic acid or its anhydride or fumaric acid. The reaction products are tricarboxylic acids, which are referred to as maleopimaric or fumaropimaric acids. The rosin adducts have a high melting point, and their high acidity makes them reactive with many materials, such as metal hydroxides, to form resinates.

Pure calcium resinates synthesized from monomeric rosin by either the fusion method or solvent method are known to crystallize or otherwise solidify (block) during the reaction, especially at higher metal levels. However, when unmodified monomeric rosin is used, high metal contents are often needed to give sufficiently high viscosity to the resinate solu-

tion. The target value of the solution viscosity of the resinate varies, depending on the application. According to Jilek (1976), the solutions of the calcium resinates to be used as an ink vehicle should have a viscosity of about 500 mPa/s at 50 wt. % resinate concentration. In the present work the target value for the solution viscosity of the Ca/Mg-resinate is in the range of 50 to 100 mPa/s at 50 wt. % resinate concentration in toluene.

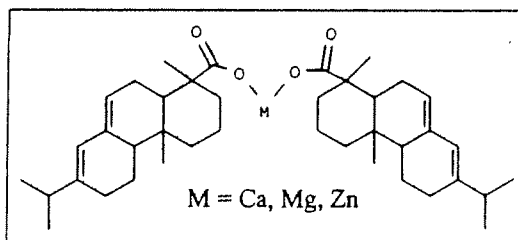


Figure 1. Resinate molecule scheme.

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The difficulty during the resinate-synthesis-by-fusion method is the change in the physical properties of the resinate, especially the increase in solution viscosity. During the synthesis the increase in solution viscosity at a given resinate concentration turns almost exponential at a specific reaction time. Therefore it is difficult to control a resinate process and to obtain a product with the desired solution viscosity.

In the resinate-synthesis-by-fusion method the main reaction is resinate formation. The most important side reaction is the decarboxylation of rosin acids forming neutral rosin oil. Other side reactions are the isomerization and polymerization (mainly thermal dimerization) of rosin acids. The isomerization and polymerization mechanisms of rosin acids have been studied by Sinclair et al. (1970) and Zinkel (1983). In this context, however, these side reactions have minor importance, because isomerization does not have a direct effect on the viscosity and polymerization occurs only to a small extent. Therefore, these side reactions are neglected in this study. The decarboxylation of rosin acids is not as well studied as the other side reactions, although its effect on viscosity is more important. It increases the resinate concentration in the reaction mixture when the neutral rosin oil vaporizes from the system.

Due to the lack of detailed knowledge of the phenomena on a molecular level, the chemical factors affecting the macroscopic properties of the reaction mixture, especially viscosity, are unexplained. The viscosity problems related to the blocking phenomenon have been observed by some authors (Petrone, 1971; Panda and Panda, 1985), but no explanation of the cause of this kind of behavior has been published. In this article, the reason for abrupt viscosity increase in the resinate solution after the critical resinate concentration is explained by resinate molecular interactions and excluded volume effects.

Simple kinetic measurements in the resinate synthesis are generally based on acid number determinations, conventionally by off-line titration with KOH. The titration gives the overall state of the system: the progress of the resinate reaction and the decarboxylation of rosin acids. In this article, an attempt is made to model the solution viscosity increase during resinate synthesis on the basis of acid number titration data. A simple mathematical model with two parameters is derived in order to be able to control the resinate process and the viscosity of the product.

Experimental Section

Synthesis procedure

Ca/Mg-resinates were synthesized by the fusion method in a 500-mL oil-heated batch-reactor vessel. The reaction mixture was stirred with a plate impeller. Nitrogen was continuously bubbled through the system. Syntheses were made from tall oil rosin (acid number 165 mg(KOH)/g) and from pure abietic acid (> 85%, Sigma, acid number 185 mg(KOH)/g). *Pro analysis* quality $\text{Ca}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, and $(\text{CH}_3\text{COO})_2\text{Ca}$ were used as the reactive metal salts. The molar ratio 6.3:1 of Ca to Mg was used in the syntheses.

The rosin or the abietic acid was melted in the vessel at 235°C and the metal salts were gradually added to the rosin melt over 2 h. Then the temperature was increased to the

reaction temperature, which was 245–265°C, depending on the synthesis. Reaction time was 5–6 h. Without taking into account the mass loss during the syntheses, the total theoretical metal contents calculated for the product were 3.4–3.5 wt. %.

In the modified resinate syntheses, rosin was fortified to the acid number level 190 mg(KOH)/g using either maleic acid anhydride or fumaric acid. The fortification of rosin was carried out at 195°C and the reaction time was 2 h. In addition two different modifiers and their effect on the viscosity of the resinate were tested. Polyethenevinylacetate copolymer (EVA, $M = 50,000$ g/mol) was added in the amount of 1.5 wt. % and 5.0 wt. % of rosin to the fortified rosin melt after one hour at 195°C. Butyl-phenolformaldehyde resin (PFR) was added in the amount of 5.0 wt. % and 10 wt. % of rosin to the unfortified rosin melt at 180°C. The reaction time of PFR was 2 h. The modified resinate synthesis was also made from polymerized rosin (13 wt. % trimeric and 24 wt. % dimeric rosin acids) with a theoretical metal content of 1.8 wt. %.

Analysis

The number-average molar mass and the possible aggregation of the resinate molecules in toluene were examined with a vapor-pressure osmometer (VPO) (Knauer GmbH) using benzil as a standard. An infrared-spectrometer (NIC Nicolet SDXC FT-IR Spectrometer) equipped with a ZnSe-cuvette (0.05 mm) was used to study the intermolecular hydrogen bonds between the two free carboxylic acid groups of the resinate in toluene. The density measurements (using Anton Paar KG DMA55 Calculating Precision Density Meter) were carried out at different resinate concentrations in toluene at 25°C in order to study the contribution of the resinate concentration to nonideal mixing. An attempt was made to determine the molecular size distribution of the resinate by GPC analysis (Waters 486, eluent: tetrahydrofuran (THF), column: Ultrastaygel 100 Å, flow velocity: 0.4 mL/min, detector: UV/VIS, $\lambda = 268$ nm).

The progress of the synthesis was followed by acid number titrations and viscosity measurements. The titration was carried out in a neutralized toluene-ethanol solution of the resinate with 0.2 M KOH using phenolphthalein as an indicator. The melt and solution viscosities of the resinate were measured by a Brookfield Digital DVII Viscometer.

Molecular Interpretation of Critical Resinate Concentration

Solution viscosity at different resinate concentrations in toluene

The toluene solution viscosity of the Ca/Mg-resinate was observed to be highly dependent on the mass concentration (Figure 2a). The increase in viscosity turned almost exponential after a specific concentration value. Therefore this concentration was determined as the critical concentration of the resinate, c_{crit} . The change in viscosity dependence on resinate concentration implies a transition from a dilute solution to a concentrated region, where molecular interactions have a stronger influence on viscosity.

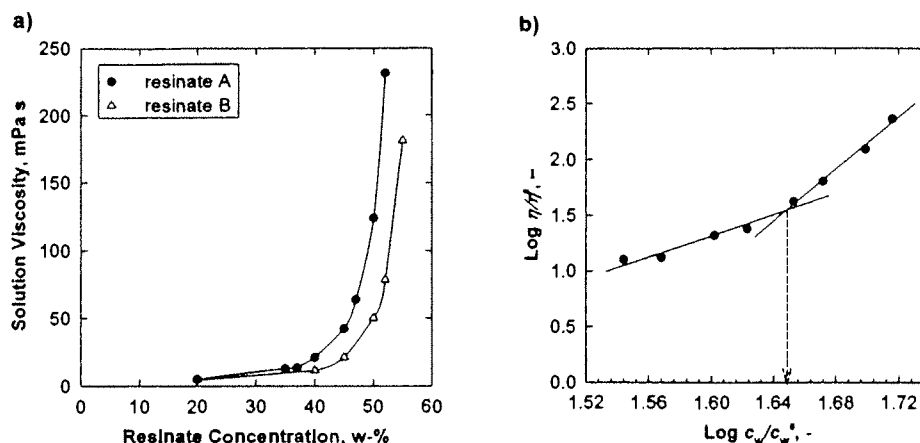


Figure 2. (a) Viscosity Increase in toluene solutions of two different Ca/Mg-resinates; (b) determination of the critical concentration for resinate A.

The critical concentration value was determined based on a log-log plot of viscosity and concentration data for resinate A (Figure 2b). The intersecting lines were statistically calculated using least-square errors criteria to separate the points belonging to each line. The values of the critical concentrations for the resinates A and B with different acid contents were 44.6 wt. % and 48.1 wt. %, respectively.

Molecular interactions in the critical concentration region

Molecular interactions were studied at different resinate concentrations in toluene in the critical concentration region. The measurements were carried out using an FTIR, a vapor-pressure osmometer, and a density analyzer. The sample was the fortified Ca/Mg-resinate with an acid content of 1.22 mmol/g and $c_{crit} = 48.1$ wt. %.

FTIR Measurements. Free carboxylic acids tend to associate with another acid group forming intermolecular hydrogen bonds between molecules in nonpolar solvent. This is observed by FTIR measurements. FTIR analyses of the resinate were carried out in toluene solution at concentrations at 40–58 wt. %. There were no differences in the spectra of the resinates when the concentration of the sample increased. Even in the most dilute solution, almost all of the rosin acid groups in the resinate had formed hydrogen bonds. Because the molar absorbance of the acid groups did not depend on the concentration of the resinate, the association of rosin acids did not affect the critical resinate concentration value.

VPO Measurements. Another form of possible molecular interaction, in addition to association of acid groups through hydrogen bonding, is the molecular aggregation of different molecules in the reaction mixture. In order to observe possible aggregation of the molecules in toluene solution of the resinate the VPO measurements were carried out at two different temperatures, 25°C and 45°C. The vapor pressure of the resinate solutions was measured using pure solvent (toluene) as a reference system. The VPO method is based on accurate measurement of temperature difference, which is recorded as resistance difference, ΔR .

Number-average aggregation numbers for the resinate solutions were calculated according to Eqs. 1 and 2 derived by J. Paatero (1975):

$$\bar{n} = \frac{K'' x_1}{2(1 - x_1)\Delta R} \left(1 - \frac{2\Delta R}{K''} + \sqrt{1 + \frac{2\Delta R}{K''}} \right), \quad (1)$$

where x_1 denotes the mole fraction of the sample, K'' is the calibration constant, and ΔR is the measured resistance difference, both expressed in mm. The calibration constant was measured by using benzil as a standard. The slope of the line (ΔR vs. mole fraction of benzil) gave the calibration constant.

The solution of \bar{n} from Eq. 1 is iterative, because the sample concentration is dependent on the number-average aggregation number according to

$$x_1 = \frac{c_1/\bar{n}}{c_2 + c_1/\bar{n}}, \quad (2)$$

where c_1 and c_2 denote the analytical concentrations of the solute and the solvent, respectively.

The number-average molar mass of the resinate was determined by VPO using THF as the solvent. THF is more polar than toluene, and therefore the use of THF hinders hydrogen bonding between acid groups, giving a more accurate value for the number-average molar mass of separate molecules. Compared to the theoretical value of the molar mass of calcium abietate (640 g/mol), the measured value for number-average molar mass of the resinate ($\bar{M}_n = 890$ g/mol) containing free rosin acids 1.22 mmol/g is relatively high. This is explained by possible resinate polymers in the reaction mixture. The polymeric resinate molecules may be formed when using fortified rosin with an acid functionality of three.

The molar mass of the resinate measured in THF was used to calculate mole fractions for Eq. 1 when calculating num-

Table 1. Number-Average Aggregation Numbers for Ca/Mg-Resinate in Toluene Determined by VPO

Resinate Conc. wt. %	Aggregation No.	
	$T = 25^{\circ}\text{C}$	$T = 45^{\circ}\text{C}$
5	1.29	1.36
10	1.38	1.30
45	1.34	1.25
50	1.41	1.30
55	1.49	1.37
58	1.51	1.36

ber-average aggregation numbers for the resinate at two different temperatures in toluene (Table 1).

The aggregation number differs from one even at the lowest resinate concentration. This is explained by considering the acid concentration of the resinate, which was 1.22 mmol/g. These acid groups associate through hydrogen bonds in toluene raising the aggregation number to greater than one.

In order to obtain high accuracy, the VPO method requires that the sample droplet placed in the thermistor should be of equal size. However, this requirement was difficult to fulfill for the measured series due to the large differences in viscosities at different concentrations. Therefore, the values differ when increasing the resinate concentration. However, increasing the concentration to the critical concentration region ($c_{\text{crit}} = 48.1$ wt. %) does not affect the aggregation number. On the basis of FTIR and VPO results, it is concluded that the viscosity increase is not due to any chemical association of the resinate molecules in the solution.

Density Measurements. The general mixing rule was applied to calculate the density difference in the mixing of resinate and toluene at different mass proportions,

$$\Delta \rho_{\text{mix}} = \rho_{\text{measured}} - \rho_{\text{ideal}} \quad (3)$$

$$\rho_{\text{ideal}} = \frac{\sum x_i M_i}{\sum x_i V_{m,i}^*} \quad (4)$$

where M_i and $V_{m,i}^*$ denote the molar mass and molar volume of the pure component i , respectively, and x_i is the mole fraction of i in the mixture. The ideal density (Eq. 4) can also be calculated from the total mass and volume based on mass fractions and the densities of the pure components (resinate 952 kg/m³ and toluene 862 kg/m³).

The mixture behaves like an ideal solution when the mixing parameter $\Delta \rho_{\text{mix}} = 0$. In order to reveal the contribution of the resinate concentration to nonideal mixing, the value of the mixing parameter was proportioned to the resinate concentration (Figure 3). The figure implies that the relative mixing parameter is independent of concentration at low resinate concentrations in toluene. The increase after 20 wt. % resinate concentration implies a transition toward more dense packing of the molecules in the mixture.

Based on the FTIR, VPO, and density results it is concluded that there are two concentration regimes in studying the viscosity behavior of the resins. The linear regime, where the resinate concentration is smaller than c_{crit} , and the nonlinear viscosity increase regime ($c > c_{\text{crit}}$), where the molecules form a sufficiently dense packing for increased molecular interactions.

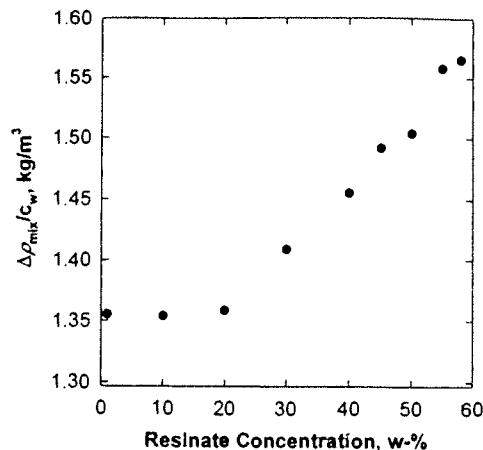


Figure 3. Relative mixing parameter in the density measurement of Ca/Mg-resinate in toluene at 25°C.

Kinetic and Viscosity Model for the Syntheses

General progress of the syntheses

Resinates were synthesized from pure rosin and fortified abietic acid and rosin. In addition EVA and PFR were used in order to control the increase in the viscosity to the target level.

It is not possible to synthesize Ca/Mg-abietate by the fusion method at 265°C using the theoretical metal content of 3.5 wt. % for the product due to the high viscosity, which prevents efficient mixing. Therefore the reference syntheses were made from fortified AA and from fortified rosin (Figure 4). In the abietate synthesis a strong viscosity increase was observed within a few hours of reaction time. With fortified rosin this phenomenon of viscosity increase was considerably weaker.

Figure 4b shows (note that $t = 0$ h is the time when the temperature had reached 265°C) that during the synthesis from fortified abietic acid the acid number values were much lower than the theoretical value. In the case of rosin the theoretical acid value is not reached until 4 1/2 h reaction time, because the resinate reaction is not completed at time $t = 0$ h. The theoretical value is based on the stoichiometric reaction (1:2) between the metal salt and the rosin acid without taking into account the decarboxylation reaction. Thus the difference between the theoretical and measured values gives the relative amount of decarboxylated rosin in the reactor, when the neutral rosin oil has almost completely vaporized from the system.

Gel permeation chromatography (GPC) analysis shows (Figure 5) that abietic acid polymerizes more than rosin during the synthesis. Thermal dimerization was observed only to a small extent in the resinate synthesis from rosin. The rosin acid content and the amount of abietic-type rosin acids affects the dimerization of rosin acids through double bonds. The high content of dehydroabietic acids in rosin prevents dimerization, because these acids do not have a conjugated

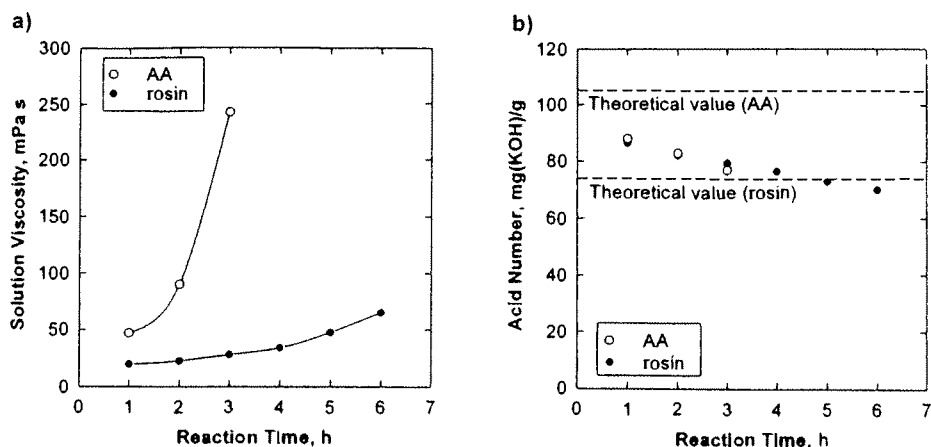


Figure 4. Syntheses of Ca/Mg-resinates from fortified abietic acid (AA) and fortified rosin at 265°C. (a) Viscosity of 50 wt. % resinate toluene solution. (b) Acid number of the resinate.

diene structure. Only a relative amount of decarboxylated rosin acid is observed in GPC grams, because the neutral rosin oil has almost completely evaporated from the system.

Melt Viscosity Increase During the Synthesis. The viscosity of the 50 wt. % toluene solution of the resinate is usually measured when monitoring the progress of the reactions. The relation between the melt viscosity (measured at 200°C) and the toluene solution viscosity (at 25°C) was studied for the fortified Ca/Mg-resinate (Figure 6). Increase in melt viscosity of the resinate indicates the growth of molecular size.

Effect of Fortification of Rosin. The rosin is fortified in order to stabilize the viscosity increase and to obtain a higher softening point for the resinate to be used as an ink vehicle.

The more complete resinate reaction when using fortified rosin was observed from the acid number values (Figure 7b). The values did not reach the theoretical value during the syn-

thesis without fortification in 6 h, which was probably due to dispersion problems with the slaked lime in the reaction. Similar behavior was reported by Oldring and Hayward (1987), when the value of the theoretical acid number was low (below 40 mg(KOH)/g). Calculated from the measured acid number values after 15-min reaction time, only 75% of the added metal salts had reacted, assuming that decarboxylation had not occurred. When fortified rosin was used, the resinate reaction was 90% completed after 15 min.

In the synthesis using fortified rosin the critical concentration value was 47.7 wt. % after 6 h, and without fortification it was 46.2 wt. %.

Effect of Reaction Temperature. In the syntheses at lower reaction temperatures it was observed that the viscosity increase remained almost linear during the 6 h reaction time (Figure 8). This was due to the hindering effect of the lower

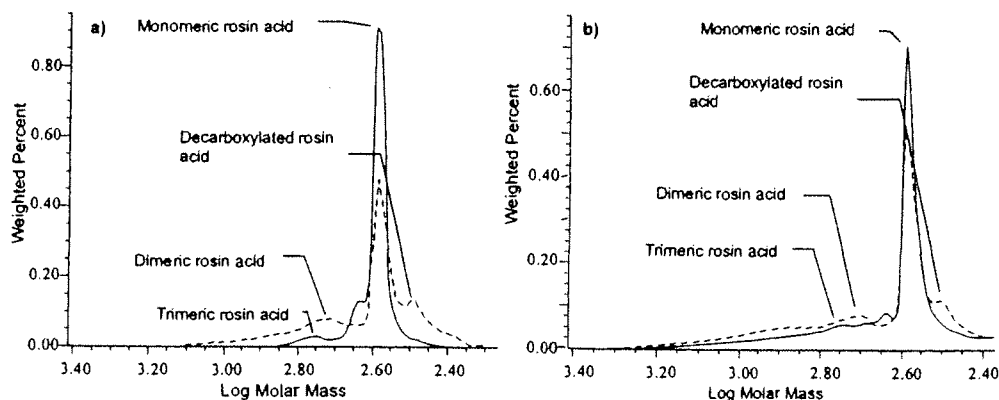


Figure 5. Effect of polymerization of rosin acids on molar-mass distribution of the resinate measured by GPC. (a) — fortified AA; - - - Ca/Mg-abietate ($T = 265^{\circ}\text{C}$, reaction time 3 h). (b) — fortified rosin; - - - Ca/Mg-resinate ($T = 265^{\circ}\text{C}$, reaction time 4 h).

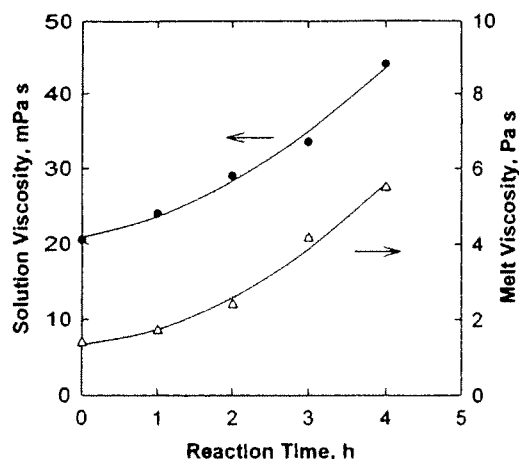


Figure 6. Melt viscosity and 50 wt. % toluene solution viscosity of fortified Ca/Mg-resinate; melt viscosity was measured at 200°C and solution viscosity at 25°C.

reaction temperature on the resinate reaction and on the decarboxylation of rosin acids observed from the acid number values of the synthesis.

The critical concentrations of the resins synthesized at different reaction temperatures were determined from the log-log plot of viscosity data at different concentrations. At the reaction temperature 265°C the critical concentration value was 47.7 wt. %, at 255°C the value was 51.6 wt. % and at the lowest temperature (245°C) the critical value was 52.5 wt. %. Because the critical resinate concentration value was greater than 50 wt. % at the two lower reaction temperatures, the viscosity increase remained linear in Figure 8a.

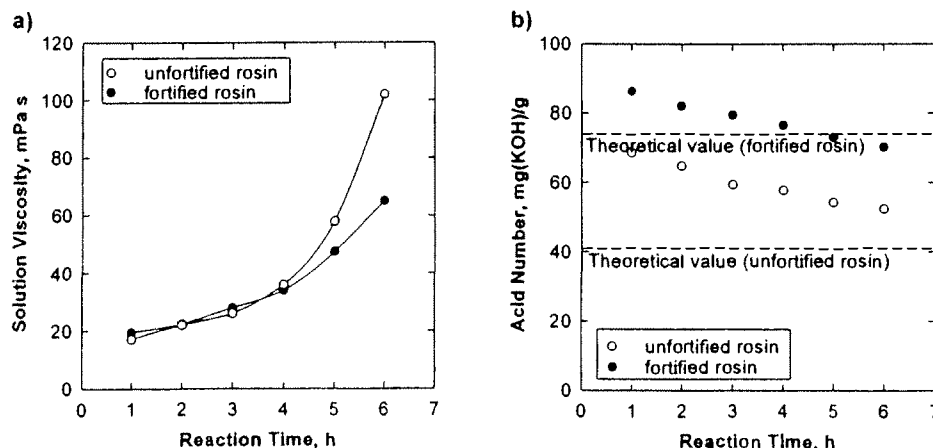


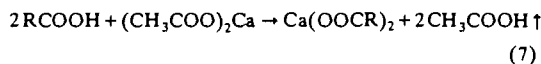
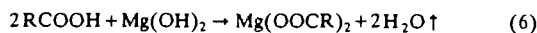
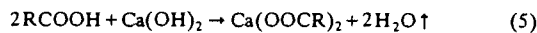
Figure 7. Syntheses of Ca/Mg-resinates from rosin and fortified rosin at 265°C.

(a) Viscosity of 50 wt. % resinate toluene solution. (b) Acid number of the resinate.

Modeling of viscosity increase

Reactions Affecting Acid-Number Value. Kinetic studies were carried out by conventional method using acid-number titration, which gives the result of the overall state of the system: the progress of the resinate reaction and decarboxylation of rosin acids.

Reactions of the acid groups during the resinate synthesis are resinate formation (5–7) and decarboxylation (8):



By assuming that water and acetic acid are completely removed from the reaction mixture due to the relatively high reaction temperature ($T = 265^\circ\text{C}$), the rate laws (Eq. 9) and (Eq. 10) are written for the irreversible resinate and decarboxylation reactions, respectively:

$$r'_A = -k'c_A^2c_B \quad (9)$$

$$r''_A = -k''c_A \quad (10)$$

where A denotes a carboxylic acid group and B is $\text{Ca}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, or $(\text{CH}_3\text{COO})_2\text{Ca}$.

Mass Balance of the Reaction System. The loss of mass during the synthesis affected the kinetic study. The loss, which was observed to be about 20% of the total mass, was mainly caused by the decarboxylated rosin vaporizing from the open reaction vessel with nitrogen. In the experimental setup the neutral rosin oil could not be collected and weighed because it either escaped through or solidified and blocked the distillation column. Calculated from the overall mass balance, it

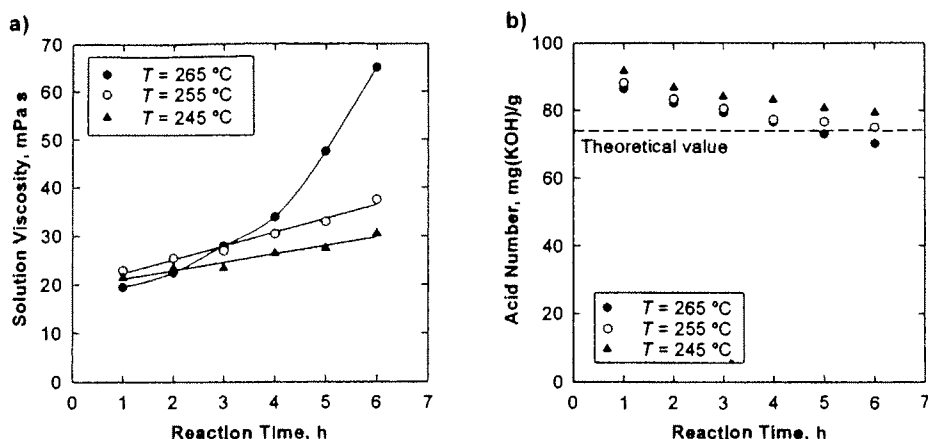


Figure 8. Syntheses of Ca/Mg-resinates from rosin at different reaction temperatures. (a) Viscosity of 50 wt. % resinate toluene solution. (b) Acid number of the resinate.

was concluded that almost all (> 95%) decarboxylated rosin acids evaporate from the system, and it was assumed that the total molar flow from the reactor consisted only of the decarboxylated rosin and carbon oxides vaporizing from the system. This simplification was done by neglecting water and acetic acid in the vaporizing flow. The total amounts of water and acetic acid are less than 5% of the total mass and it is assumed that most of them have already been vaporized when the temperature has reached 265°C ($t = 0$ h). The kinetic study of the resinate synthesis is similar to polyesterification kinetics followed by acid number titrations (Paatero et al., 1994), despite the fact that the water of the reaction is of minor importance in the resinate synthesis.

During the synthesis of the resinates in the fusion method, the mass balances of the compounds in the reaction vessel can be written as

$$r_i m = \dot{n}_{i,v} + dn_i/dt, \quad (11)$$

where r_i denotes the generation rate ($i = \text{RCOOH}$) expressed in mol/(min kg solution), m is the mass of liquid in the reactor, n_i is the amount of compound i in the reactor, and $\dot{n}_{i,v}$ is the molar flow of i leaving the reactor by vaporizing. The amounts and flows of substance are expressed with the concentrations (c_i), the mass of the liquid (m), and the vaporizing mass flow (\dot{m}_v):

$$n_i = c_i m \quad (12)$$

$$\dot{n}_{i,v} = c_{i,v} \dot{m}_v, \quad (13)$$

where c_i and $c_{i,v}$ denote the concentrations in the reactor and vaporizing stream, respectively. Furthermore, the mass in the reactor, the mass of the vaporized substance (m_v), as well as the mass and molar flow (\dot{n}_v) are related by

$$-dm/dt = dm_v/dt = \dot{m}_v = \dot{n}_v M_v, \quad (14)$$

where M_v is the molar mass of the vaporized substance. It is

the molar mass of rosin acid (302 g/mol) according to the decarboxylation reaction (Eq. 8). By assuming that the total molar flow from the reactor equals the decarboxylated rosin and carbon dioxide evaporating from the system, the molar flow is expressed as

$$\dot{n}_v = m r'_A, \quad (15)$$

where A denotes the acid group. After inserting Eqs. 12–15 into the balance equation (Eq. 11) and performing the differentiation, the following equation is obtained

$$dc_A/dt = r'_A + r''_A + c_A r'_A M_v. \quad (16)$$

Because resinate reaction is fast, it is assumed that $r'_A \approx 0$ when the temperature has reached 265°C ($t = 0$ h), and so Eq. 16 is written by inserting Eqs. 9 and 10 as

$$dc_A/dt = -k'' c_A - k'' M_v c_A^2, \quad (17)$$

which is rewritten as

$$dc_A/dt = -k'' c_A (1 + M_v c_A). \quad (18)$$

According to Eqs. 17 and 18, the total reaction order is between one and two depending on the $M_v c_A$, the value of which was between 0.5 and 0.3 during the different syntheses. Since the final aim is to obtain a viscosity model, it is sufficient to include the kinetic model in a simplified form. The simplified model is tested by fitting the data to the first- (Eq. 19) and second-order (Eq. 20) rate equations linearized by integration:

$$\ln(c_{A,0}/c_A) = k'' t \quad (19)$$

$$c_{A,0}^{-1} - c_A^{-1} = k'' t. \quad (20)$$

The experimental kinetics fit reasonably well into both of the preceding linear rate equations, but the average fit was better when using the second-order rate law (Eq. 20). Figure

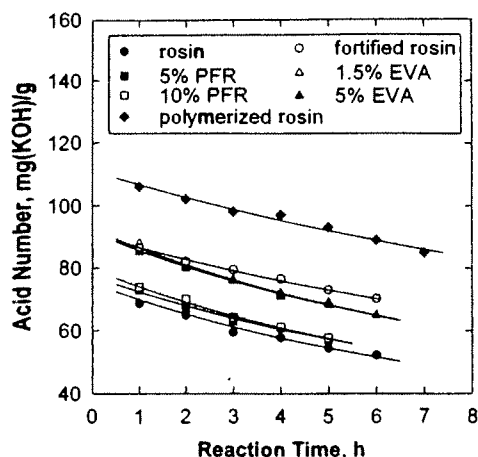


Figure 9. Empirical values and fit of the second-order rate model for acid numbers in the syntheses of Ca/Mg-resinates at 265°C from rosin, from PFR-modified rosin, from polymerized rosin, and from fortified rosin with EVA additions.

9 shows the data fit for the second-order rate equation. The lowest acid number values for resinates are obtained using rosin without fortification, because the fortification of rosin affects the initial acid number in the syntheses. The highest values are in the synthesis using polymerized rosin, because the theoretical metal content of the synthesis was only half that used in the other syntheses.

From Eq. 20 the apparent reaction-rate constants were determined for the resinate synthesis made from fortified rosin at different temperatures. The corresponding Arrhenius plot is shown in Figure 10, from which the obtained apparent activation energy was 60.1 kJ/mol.

Viscosity Dependence of Acid Concentration. The empirical correlation between the viscosity of 50 wt. % toluene solution of the resinate and the acid concentration in the reaction vessel was derived as

$$\frac{1}{\eta} = a' + b'c_A^{-1}. \quad (21)$$

By combining Eqs. 20 and 21, Eq. 22 is obtained:

$$\frac{1}{\eta} = (a' + b'c_{A,0}^{-1}) + (b'k'')t, \quad (22)$$

which can be rewritten by lumping the constants as

$$\frac{1}{\eta} = a + bt. \quad (23)$$

This simple two-parameter model provides a good description for the viscosity of the resinate solution as a function of reaction time. Parameter a describes the viscosity level at the reaction time $t = 0$ (the smaller the value of a is, the bigger the initial value of the viscosity). Parameter b includes the

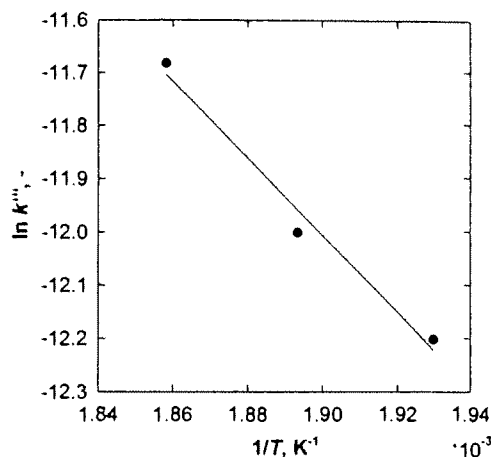


Figure 10. Determination of apparent activation energy for reactions in the synthesis of Ca/Mg-resinate from fortified rosin.

rate constant from the kinetic model, thus illustrating the rate of the viscosity increase. Figure 11 illustrates the fit of the model (Eq. 23) for the resinate syntheses with different modifications.

The fortification of the rosin affects the shape of the viscosity curve (Figure 11a). In EVA additions rosin was fortified, and in modification with PFR the fortification was not done. Viscosity increase is weaker with fortified rosin independent of the viscosity level.

Figure 11a indicates that the resinate syntheses from unmodified rosin and fortified rosin, as well as those of slightly modified rosin, have good correlations. It is obvious that severe modifications (Figure 11b) change the viscosity increase in resinate syntheses, because factors other than resinate reaction and decarboxylation also affect viscosity. In the synthesis using polymerized rosin, the high viscosity values were partly due to the rosin dimers present in the reaction mixture. PFR can react with rosin acids and hence increase the viscosity. Addition of EVA changes the relation of viscosity to acid concentration because of the higher viscosity level due to the macromolecules being added to the reaction mixture.

The models (Eqs. 21 and 23) can be used in process control. The independent parameters a' , b' , a , and b can be calculated based on acid number and viscosity samples at two different reaction times during the progress of the reactions. Parameter determinations can be done for several process batches, with different amounts of Ca and Mg being added and with different grades of raw material (rosin) being used. So the viscosity increase of the resinate solution and the total reaction time of the batch can be estimated.

Determination of t_{50} from the Viscosity Model. The reaction time at which the viscosity increase changes is denoted by t_{50} . This critical time can be predicted from the viscosity model by dividing Eq. 23 by time t , obtaining function $f = \eta/t = [t(a + bt)]^{-1}$, which has an inflection point at t_{50} . By forming the first time derivative (f') of this function and by calculating t_{50} from the zero point of f' , the following equation (Eq. 24) is obtained:

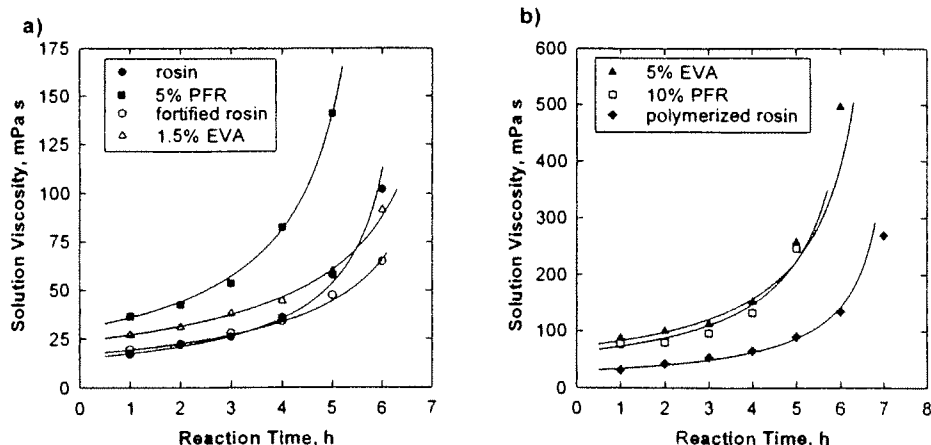


Figure 11. Viscosity increase in 50 wt. % toluene solution of Ca/Mg-resinates and modified resinates during synthesis at 265°C.

Lines are calculated according to the viscosity model (Eq. 23).

$$t_{50} = -\frac{1}{2} \frac{a}{b}, \quad (24)$$

which includes the parameters a and b from the viscosity model (Eq. 23). The t_{50} values in Table 2, calculated according to Eq. 24, indicate that fortification of rosin tends to increase the critical reaction time.

Conclusions

To study the molecular background for the abrupt solution-viscosity increase during the fusion synthesis of Ca/Mg-resinates, the solution viscosity of resinates was studied at different concentrations in toluene. It was observed that the viscosity increase turns almost exponential at a critical resinate concentration, denoted here by c_{crit} . This phenomenon is explained by resinate molecular interactions and excluded volume effects, when molecules are packed sufficiently densely in the solution.

The concept of critical resinate concentration was applied to explain the nonlinear viscosity increase in 50 wt. % toluene solution of the resinate during the syntheses. The abrupt solution-viscosity increase indicates the time, denoted by t_{50} , when the critical concentration of the resinate has reached the value of $c_{crit} = 50$ wt. %. A simple mathematical model with two parameters was derived from apparent reaction kinetics for the solution viscosity increase in the resinate

syntheses (Eq. 23). The model provides a good description for the viscosity increase, not only for the synthesis of Ca/Mg-resinates made from rosin but also for the syntheses of slightly modified resinates with higher viscosity. The viscosity model can be applied to control the resinate process and to predict the t_{50} time (Eq. 24) of the syntheses.

Notation

- a' = parameter in Eqs. 21 and 22, $(\text{Pa} \cdot \text{s})^{-1}$
- b' = parameter in Eqs. 21 and 22, $\text{g/kg} (\text{Pa} \cdot \text{s})^{-1}$
- c_0 = resinate mass fraction in toluene, wt. %
- c_0^* = unit concentration, wt. %
- E = activation energy, J/mol
- k' = reaction-rate constant of the resinate reaction, $\text{kg}/(\text{mol} \cdot \text{min})$
- k'' = reaction-rate constant of the decarboxylation reaction, min^{-1}
- k^* = apparent reaction-rate constant, $\text{kg}/(\text{mol} \cdot \text{min})$
- η^0 = unit viscosity, $\text{Pa} \cdot \text{s}$

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Table 2. Critical Reaction Times of the Resinate Syntheses

Resinate Synthesis Using	t_{50}
Rosin	3 h 27 min
5% PFR modified rosin	3 h 12 min
10% PFR modified rosin	3 h 35 min
polymerized rosin	3 h 45 min
Fortified rosin	4 h
1.5% EVA addition to fortified rosin	4 h 10 min
5% EVA addition to fortified rosin	3 h 42 min

II

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Resination and Decarboxylation Reactions in Fusion Synthesis of Ca-Resinates

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The reaction steps in fusion synthesis of Ca-resinates include a fast, irreversible resination reaction and a slow decarboxylation of rosin acids. The kinetics of the reactions was studied separately in a laboratory scale batch reactor. The kinetic data were obtained by acid number titrations and FTIR measurements. Resination was observed to be a fast irreversible reaction in the temperature range 190 to 235°C. Rate equations for the decarboxylation reaction were derived based on plausible mechanistic reaction steps of free and solvating rosin acids. The parameters of the rate equations were estimated for syntheses at different reaction temperatures (265 to 285°C) and the kinetic model was successfully applied to predict the experimental kinetics of rosin acid decarboxylation.

Les étapes de réaction dans la synthèse de résinats de Ca incluent une réaction de résination rapide et irréversible et une lente décarboxylation des acides de rosin. La cinétique des réactions a été étudiée séparément dans un réacteur discontinu à l'échelle de laboratoire. Les données cinétiques ont été obtenues par titration des nombres d'acides et des mesures FTIR. On a observé que la résination était une réaction irréversible rapide dans la gamme de températures comprises entre 190 et 235°C. Des équations de vitesse pour la réaction de décarboxylation ont été établies à partir d'étapes de réaction mécanistiques plausibles d'acides de rosin libres et de solvation. Les paramètres des équations de vitesse ont été estimés pour les synthèses à différentes températures de réaction (de 265 à 285°C) et le modèle cinétique a été appliqué avec succès dans la prédiction de la cinétique expérimentale de décarboxylation des acides de rosin.

Keywords: Ca-resinate, fusion synthesis, rosin acid, decarboxylation, FTIR.

Ca-resinates are the calcium salts of rosin acids and they are used as binders in publication gravure inks. The resinates are industrially produced either by solution or fusion methods. In fusion synthesis, calcium hydroxide and calcium acetate are often used as the reactive metal salts. The reaction steps include a fast irreversible resination reaction and a slow decarboxylation reaction of rosin acids forming neutral rosin oil. In addition, the side reactions, isomerization and polymerization (mainly thermal dimerization) of rosin acids take place (Sinclair, 1970 and Zinkel, 1983).

The target value for the solution viscosity of the resinate varies, depending on the application. According to Jilek (1976), solutions of calcium resinates to be used as an ink vehicle should have a viscosity of about 500 mPa·s, at 50 wt% resinate concentration. In order to obtain the target solution viscosity of the product, it is necessary to increase the resinate concentration during the synthesis.

In fusion synthesis, the resination reaction cannot occur to the desired level due to the blocking of the unreacted Ca(OH)₂ and problems in increased melt viscosity (Petrone, 1971; Jilek, 1976; Panda & Panda, 1985). Therefore, the viscosity is often raised to the desired level by increasing the resinate concentration in the reactor indirectly, by raising the temperature to enable the decarboxylation reaction to take place. The decarboxylation reaction is an essential reaction stage, although it has the negative consequence that it lowers the mass yield as the neutral rosin oil vaporizes from the system. In addition, the decarboxylation reaction increases the total reaction time of the resinate process.

In an earlier study on Ca/Mg-resinates by our group (Sundqvist et al., 1998) the progress of resination and decar-

boxylation reactions were not studied separately. All the kinetic experiments of the resinate synthesis were based on acid number titration with KOH. The titration gave the overall state of the system: the progress of the resination reaction and the decarboxylation of rosin acids. The solution viscosity was observed to be highly dependent on resinate concentration and the increase in viscosity became almost exponential after a specific concentration value, denoted by the critical resinate concentration, c_{crit} . A simplified second order semi-empirical kinetic model for the decarboxylation reaction was successfully applied to derive a model for the viscosity of 50 wt% toluene solution of the resinate during fusion synthesis. In this paper, the aim is to adjust the kinetic model by taking into account the decarboxylation reaction mechanism.

In the present work, the resination and decarboxylation reactions are studied separately in the synthesis of Ca-resinates by the fusion method. The mass balance is calculated from the resinate concentration increase. A reaction mechanism for the rosin acid decarboxylation is derived based on the analysis of the free and solvating rosin acid concentrations in the reaction milieu. The kinetic model is deduced on the basis of the reaction mechanism and the model is applied to determine the kinetic parameters for the decarboxylation reaction.

Experimental

SYNTHESES PROCEDURE

Synthesis of Ca-resinate by fusion method

Ca-resinates were synthesized by the fusion method in a 300 mL batch reactor vessel. The reaction mixture was stirred with a four blade impeller. Nitrogen or carbon dioxide was continuously bubbled through the reaction mixture. The syntheses were made from tall oil rosin (acid number

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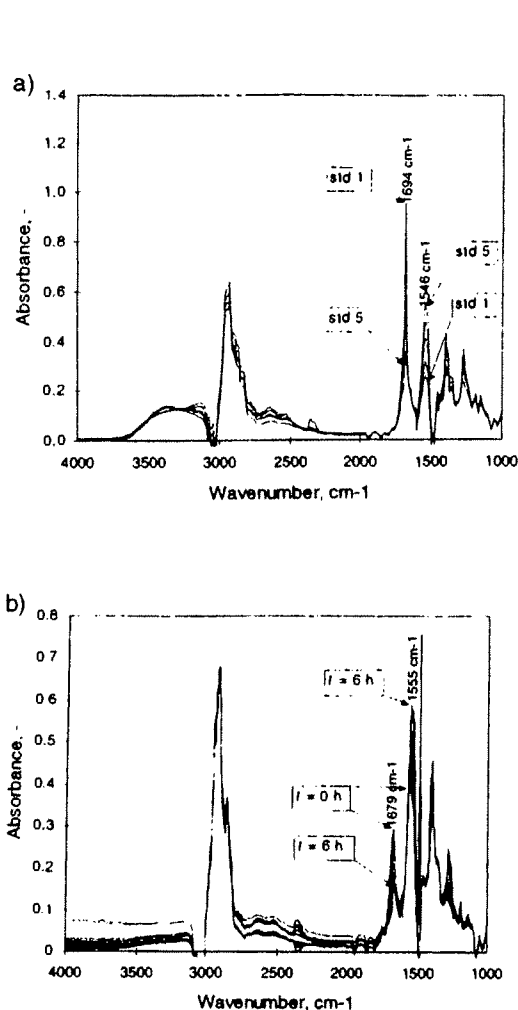


Figure 1 — a) FTIR spectra of the mixture of Ca-abietate and abietic acid; b) FTIR spectra of the Ca-resinate during synthesis at 265°C.

164 mg(KOH)/g). Pro analysis quality $\text{Ca}(\text{OH})_2$ was used as the reactive metal salt. In the reference synthesis the amount of $\text{Ca}(\text{OH})_2$ was 6.0 wt% of rosin. In the syntheses demonstrating the kinetic model at different reaction temperatures, the amount of $\text{Ca}(\text{OH})_2$ was equal to the amount required to obtain the theoretical acid value 70 mg(KOH)/g, calculated for the product.

The rosin was melted in the vessel at 235°C and the metal salt was gradually added to the rosin melt. The temperature was then raised to the reaction temperature (265°C). The reaction time was 6 h in the reference synthesis and 5 h in the demonstrating syntheses.

Synthesis of Ca-abietate by solution method

Ca-abietate was used as the calibration standard for the FTIR analyses, and it was synthesized from pure abietic acid

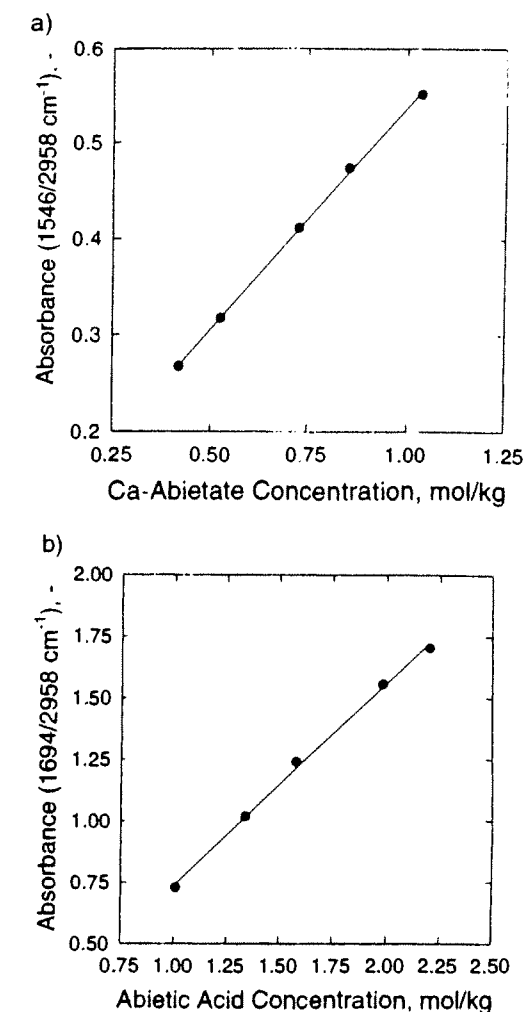


Figure 2 — Relative FTIR absorbances in toluene; a) Ca-abietate; b) Abietic acid associated to dimers.

at room temperature according to the inverse addition order method introduced by Jilek (1976). $\text{Ca}(\text{OH})_2$ was suspended into toluene, and the abietic acid toluene solution was gradually added to the stirred suspension. The stoichiometric amount of $\text{Ca}(\text{OH})_2$ was used to make 30 wt% Ca-abietate toluene solution. The product was not completely soluble in toluene due to the high metal content. The unreacted $\text{Ca}(\text{OH})_2$ was washed and filtered from the Ca-abietate with toluene. The acid number of the synthesized Ca-abietate was 11.6 mg(KOH)/g which equals a $\text{Ca}(\text{OH})_2$ conversion of 97.8%.

ANALYSIS

Potentiometric titration

According to standard ASTM D803-83 (1987), the acid number titration of the resinate is to be carried out in neutral-

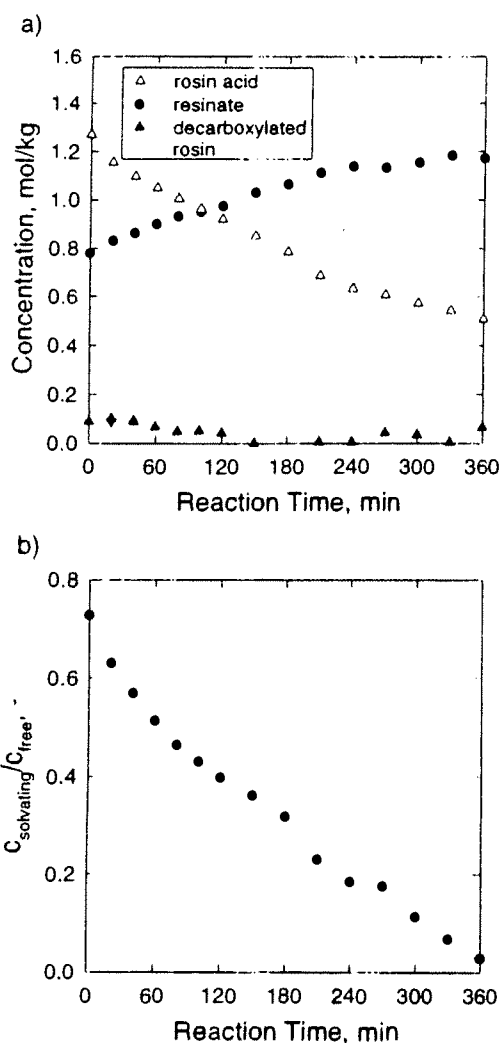


Figure 3 — Decarboxylation reaction stage in the reference synthesis at 265°C; a) Concentrations of the compounds; b) Concentration ratio of solvating to free rosin acids.

ized toluene-ethanol solution with KOH using phenolphthalein as an indicator. In this study, however, the potentiometric titration of the acid concentration with 0.2 M KOH was carried out with a Mettler Toledo DL25 Titrator using a DG111-SC electrode.

FTIR analysis

A Perkin Elmer 2000 Infra-Red-Spectrophotometer equipped with a CaF_2 transmission cuvette (0.05 mm) was used to determine the resinate concentration during the syntheses. The rosin acid concentration for the acids being associated to dimers in toluene could also be measured. The sample was 15 wt% toluene solution of the resinate. Mixtures of the Ca-abietate and pure abietic acid were used as standards for the composition of the reaction mixture.

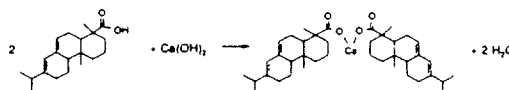


Figure 4 — Resination reaction of abietic acid.

Results and discussion

CHEMICAL COMPOSITION OF THE REACTION MIXTURE

In earlier published studies, the resinate concentration of the reaction mixture had not been analyzed because no reliable analytical method had been available. It has been difficult to make appropriate standards for the relatively complex reaction media. The composition of the reaction mixture had been characterized only by acid number determinations. In this paper, using the mixture of abietic acid and Ca-abietate as the standard, a method for FTIR measurement (Figure 1) of the concentrations of Ca-resinates and associated dimeric rosin acids in toluene is introduced.

The spectra of the standards in 15 wt% toluene solution show Ca-abietate absorption (Figure 1a) at the wavenumber 1546 cm^{-1} , while Ca-resinate (Figure 1b) absorbs at 1555 cm^{-1} . Figure 1a shows only the dimeric forms of abietic acid (1694 cm^{-1}) and all the abietic acids are assumed to form dimers in toluene. Some moisture, due to residual reaction water, is observed in the wavenumber region of 3600 to 3100 cm^{-1} .

The relative absorbances of the mixture of Ca-abietate and abietic acids in the 15 wt% toluene solution are shown in Figure 2. The absorbances have been corrected to the same base line using CH_3 -absorption at 2958 cm^{-1} . Figure 2 indicates that the lines can be used to determine the resinate concentration and the concentration of free rosin acids (capable of associating to dimers in toluene) in the reaction mixture.

Solvating rosin acids

In fusion synthesis of resinates, as a result of the interaction between the solvent (rosin acid) and the solute (resinate), the solvent molecules may become linked to the dissolved resinate molecules. The solvation phenomenon is assumed to explain the fact that all the acids titrated are not free to associate to dimers in 15 wt% toluene solution analysed by FTIR. Therefore, they do not show an absorption band in the spectra (Figure 1).

The concentration of free rosin acids was determined by FTIR measurements, and the concentration of solvating acids was then calculated based on the acid value titration of the whole acid content. Figure 3 shows the concentration changes of the reaction components and the ratio of the concentrations of solvating to free rosin acids during the reference synthesis. Reaction time $t = 0\text{ h}$ is the time when the temperature has reached 265°C . At that time, the resination reaction is regarded as completed and the decarboxylation reaction takes place. The decrease in the concentration ratio of solvating to free acid indicates that the solvating rosin acids decarboxylate more rapidly than the free rosin acids.

RESINATION REACTION AND THE MASS BALANCE OF THE SYSTEM

The resination reaction (Figure 4) was observed to be a fast irreversible reaction at a temperature range of 190 to 235°C . The reaction was completed in about 15 min (Figure 5a), and at 235°C , the conversion of $\text{Ca}(\text{OH})_2$ was 97.2%. The

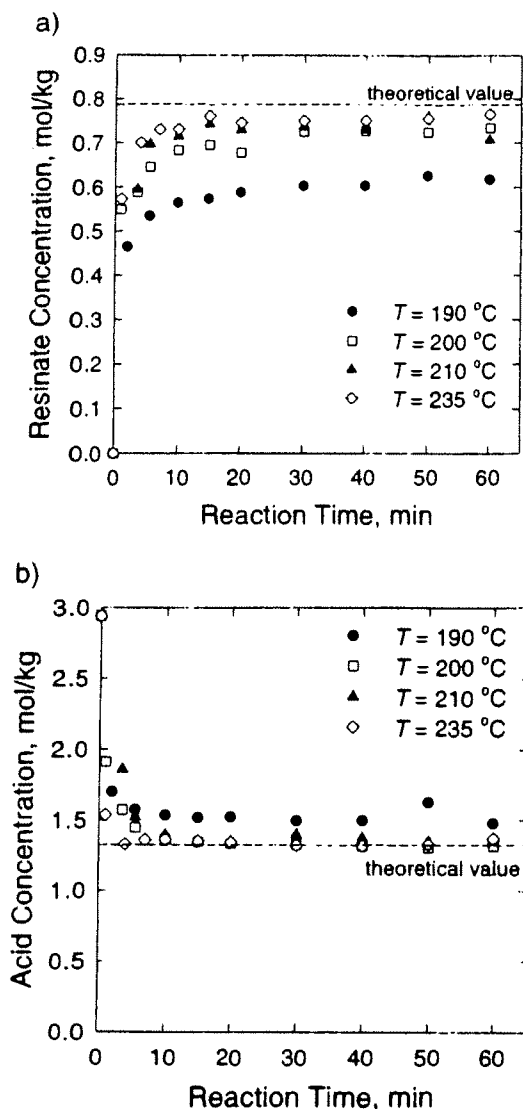


Figure 5 — Resination reaction stage in the syntheses; a) Resinate concentration measured by FTIR; b) Acid concentration measured by titration.

decarboxylation reaction is regarded as insignificant in this temperature range, as the acid value remains constant after the resination reaction is completed (Figure 5b).

Both FTIR analysis and acid number titration were used to determine the resinate concentration of the reaction mixture. The resinate concentration based on FTIR measurements (Figure 5a) is regarded as more correct than the titrated acid concentration because the unreacted $\text{Ca}(\text{OH})_2$ particles affect the titration by lowering the apparent acid value. Therefore, in Figure 5b the decrease in acid value is more rapid than the increase in resinate concentration. The differences in the extents of the resination reaction measured by FTIR, compared to that calculated from the titration data are

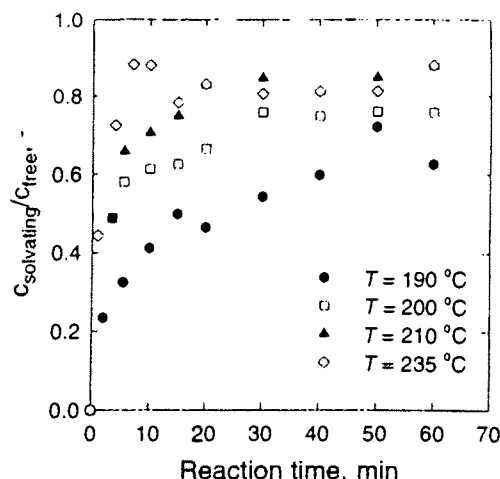


Figure 6 — Concentration ratio of solvating to free rosin acids at different resination reaction temperatures.

also explained by the effect of the residual $\text{Ca}(\text{OH})_2$ particles on the titration. At the highest reaction temperature after 15 min there was, however, no significant difference between the results of the FTIR and titration analyses.

During the resination reaction, the ratio of the amount of solvating to free rosin acids changes, depending on the reaction temperature (Figure 6). The fraction of the solvating acids increases with the increased resinate concentration at the reaction temperatures 190 to 235 °C.

In fusion synthesis, the decarboxylation reaction of rosin acids takes place after the resination reaction is completed at 235 °C, and the temperature is increased to the final reaction temperature (265 °C). The resinate concentration increases due to the vaporization of the neutral rosin oil from the reaction system. In the experimental setup, the neutral rosin oil could not be collected and weighed quantitatively, because it either solidified and blocked the distillation column, or escaped through it.

The loss of mass during the decarboxylation reaction for 6 h was measured as about 30 wt%. The mass balance was calculated by regarding the resinate amount as remaining constant. The increase in the resinate concentration (Figure 3a) indicates the relative mass loss of the system according to the mass balance equation:

$$m_1 c_1 = m_2 c_2 \quad (1)$$

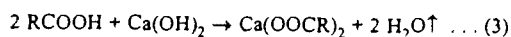
where c_1 and c_2 denote the resinate concentrations in mol/kg, and m_1 and m_2 denote the masses of the reaction mixture at the reaction times t_1 and t_2 , respectively. The relative mass loss, Δm_{rel} , is calculated from the equation:

$$\Delta m_{\text{rel}} = 1 - \frac{m_2}{m_1} = 1 - \frac{c_1}{c_2} \quad (2)$$

REACTION KINETICS

Rate laws for resination and decarboxylation reactions

The reactions of the acid groups during the Ca-resinate synthesis are the resinate formation Reaction (3) and the decarboxylation Reaction (4).



By assuming that the reaction water is completely removed from the reaction mixture because of the high reaction temperature ($T = 265^\circ\text{C}$), the rate laws (5) and (6) are written for the irreversible resination and decarboxylation reactions, respectively:

$$r_A' = -k' c_A^2 c_B \dots (5)$$

$$r_A'' = -k'' c_A \dots (6)$$

where k' is the rate constant for the resination reaction and k'' is the rate constant for the decarboxylation reaction. A denotes a carboxylic acid group and B is Ca(OH)_2 . The resination is a much more rapid reaction step than decarboxylation, therefore $k' \gg k''$.

Mass balance of rosin acids

During the synthesis of the resins by the fusion method the mass balance of the individual compound in the reaction vessel can be written as:

$$r_i m = \dot{n}_{i,v} + \frac{dn_i}{dt} \dots (7)$$

where r_i denotes the generation rate expressed in mol/(min kg solution), m is the mass of liquid in the reactor, n_i is the amount of compound i in the reactor and $\dot{n}_{i,v}$ is the molar flow of i leaving the reactor by vaporizing. The amounts and flows of substance are expressed with the concentrations (c_i), the mass of the liquid (m) and the vaporizing mass flow (\dot{m}_v):

$$n_i = c_i m \dots (8)$$

$$\dot{n}_{i,v} = c_{i,v} \dot{m}_v \dots (9)$$

where c_i and $c_{i,v}$ denote the concentrations in the reactor and vapor stream, respectively. By considering that the decarboxylation reaction is much slower than the resination reaction step, it is concluded that all the reaction water from the resination step (3) has vaporized when the temperature is 265°C . The vaporizing mass flow then consists only of decarboxylated rosin and carbon dioxide according to the reaction step (4) and the mass balance for the rosin acid is reduced to:

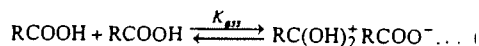
$$-\frac{dn_{\text{RCOOH}}}{dt} = k'' c_{\text{RCOOH}}^2 m \dots (10)$$

where k'' is the rate constant for the decarboxylation, and m can be calculated from the resinate concentration increase according to Equation (2).

Reaction mechanism for the decarboxylation reaction

The deduced mechanism for the rosin acid decarboxylation in the reaction mixture is based on the different reaction steps of the free and solvating rosin acids analyzed by FTIR.

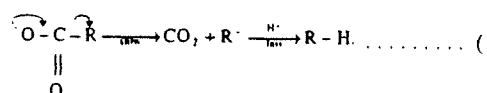
For the free rosin acids, the following protolysis equilibrium of the ion pair formation is considered:



The quasi-equilibrium approximation is applied to rapid step to express the concentration of the ion pair $\text{RC(OH)}_2^+ \text{RCOO}^-$:

$$c_{\text{RC(OH)}_2^+ \text{RCOO}^-} = K_{\text{ass}} c_{\text{RCOOH}}^2 \dots (12)$$

The decarboxylation of a carboxylate ion, RCOO^- generally believed to involve a carbanion intermediate (that subsequently acquires a proton from the solvent, another source (Sykes, 1986):



In the case of free rosin acid decarboxylation, the proton is available in ion pairs, and the delocalized structure of solvating rosin acids is the proton source in the decarboxylation of solvating acids.

Loss of carbon dioxide is normally the rate limiting step and the subsequent proton abstraction is rapid (Sykes 1986). So the rate law for decarboxylation becomes:

$$r_{\text{deca}} = k'' c_{\text{RCOO}^-} \dots (14)$$

By taking into account Equation (12) and assuming that the solvating rosin acids decarboxylate straight, according to first order kinetics with respect to the rosin acid, the decarboxylation rate of rosin acids becomes:

$$r_{\text{deca}} = k_1 c_{\text{RCOOH(s)}} + k_2 K_{\text{ass}} c_{\text{RCOOH(f)}}^2 \dots (15)$$

where k_1 and k_2 denote the decarboxylation rate constants for the solvating forms of rosin acids, RCOOH(s) , and the free acids, RCOOH(f) , respectively. K_{ass} is the equilibrium constant of the ion pair formation.

Equation (15) is comparable to the rate equation presented earlier (Sundqvist et al., 1998), in which the total reaction order for the rosin acid decarboxylation was observed to be between 1 and 2.

The reaction rate parameters are estimated separately according to the partial reaction rate Equation (16) for the solvating and the free rosin acids ($i = \text{RCOOH(s)}$, RCOOH(f)). The overall rate Equation (17) for decarboxylation is presented by means of partial reaction kinetics:

$$r_i = -\frac{1}{m} \frac{dn_i}{dt} = k_i c_i^{\alpha_i} \dots (16)$$

$$r_{\text{tot}} = r_{\text{RCOOH(s)}} + r_{\text{RCOOH(f)}} \dots (17)$$

If $r_{\text{RCOOH(s)}}$ and $r_{\text{RCOOH(f)}}$ are considered as being equal the total reaction order for rosin acids is adjusted to 1.5. Therefore, the overall fit of rosin acid decarboxylation was done according to Equation (16) and the parameter value $\alpha_i = 1.5$. Modelling of the solvating and free rosin acid decarboxylation according to Equation (16) was carried out separately with parameter values $\alpha = 1.0$ and $\alpha = 2.0$, respectively.

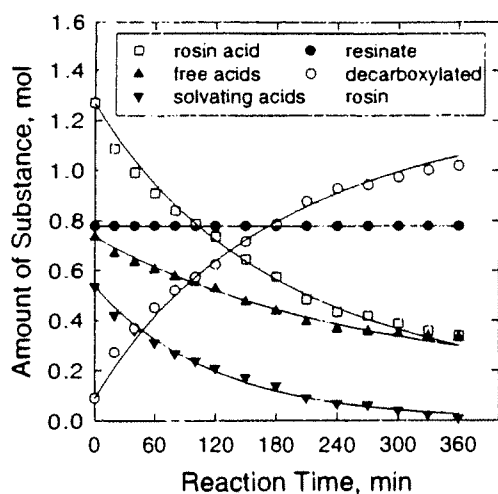


Figure 7 — Fit of the kinetic model for the decarboxylation in the reference synthesis at 265°C. The total reaction order for rosin acid decarboxylation is 1.5, partial orders are 1.0 for the solvating acids and 2.0 for the free acids.

TABLE 1
Reaction Orders and Rate Constants for the Decarboxylation Reaction of Rosin Acids in the Reference Synthesis at 265°C

	Reaction order	Rate constant (mol/kg) ^{1-α} ·min ⁻¹
Free acids	2.0	4.24 10 ⁻³
Solvating acids	1.0	8.33 10 ⁻³
Total acids	1.5	4.56 10 ⁻³

KINETIC MODEL FOR THE DECARBOXYLATION REACTION

Parameter estimation

The kinetic parameters were estimated from the differential Equation (16) using the Simflex algorithm, which is based on the simplex method introduced by Spendley et al., 1962. The differential equations were solved by means of linear multistep methods implemented in ODESSA, which is based on the LSODE software (Hindmarsh, 1983). The methods are available in the MODEST software (Haario, 1994).

The kinetic model, Equation (16), supports the deduced reaction mechanism (Figure 7) with the estimated rate constants presented in Table 1.

Testing the model

The kinetic model for the decarboxylation was tested with three demonstrating syntheses at different temperatures (Figure 8). The decarboxylation rate at the same temperature as the reference synthesis (265°C) was smaller (Table 2) than in the reference synthesis (Table 1), due to the 5% higher metal content in the demonstrating synthesis. In addition, it was observed that the decarboxylation reaction rate constant does not increase constantly with increasing temperature, when studying the solvating and free rosin acids separately. This is explained by the temperature dependence of the solvation phenomenon.

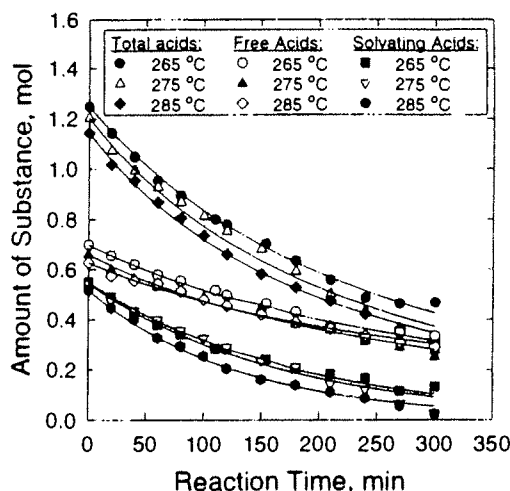


Figure 8 — Fit of the kinetic model for the decarboxylation in the demonstrating syntheses at different temperatures. Total reaction order for rosin acid decarboxylation is 1.5, partial orders are 1.0 for the solvating acids and 2.0 for the free acids.

TABLE 2
Reaction Orders, α , and Rate constants for the Decarboxylation Reaction of Rosin Acids in the Demonstrating Syntheses at Different Temperatures

Reaction temperature °C	Rate constants (mol/kg) ^{1-α} ·min ⁻¹		
	Free acids $\alpha = 2.0$	Solvating acids $\alpha = 1.0$	Total acids $\alpha = 1.5$
265	4.85 10 ⁻³	5.59 10 ⁻³	3.91 10 ⁻³
275	5.72 10 ⁻³	5.95 10 ⁻³	4.45 10 ⁻³
285	5.20 10 ⁻³	7.55 10 ⁻³	4.87 10 ⁻³

The Arrhenius parameters for the total decarboxylation reaction were calculated based on the syntheses at the reaction temperatures 265, 275 and 285°C (Figure 9). The apparent activation energy was observed to be 27 kJ/mol. The decarboxylation reaction of rosin acids was regarded as taking place in a very narrow temperature range; at 235°C no decarboxylation was observed in 60 min (Figure 5), and temperatures higher than 265°C give only a small increase in the decarboxylation reaction rate and amount. In earlier studies (Sundqvist et al., 1998) the apparent activation energy for the decarboxylation reaction was observed to be 64 kJ/mol for syntheses using fortified rosin at a temperature range of 245 to 265°C.

Synthesis in CO₂-atmosphere

The decarboxylation of rosin acids is an irreversible reaction step in a N₂-atmosphere because the neutral rosin oil and carbon dioxide escape from the system. A possible decarboxylation reaction equilibrium was studied in the synthesis of Ca-resinates in a CO₂-atmosphere. It was observed that the reaction mechanism of free and solvating rosin acids differs from the reference synthesis in the N₂-atmosphere. However, the total reaction order could be adjusted to 1.5 (Figure 10), when neglecting the scattering in the data, which could indicate a lack of fit of the kinetic model.

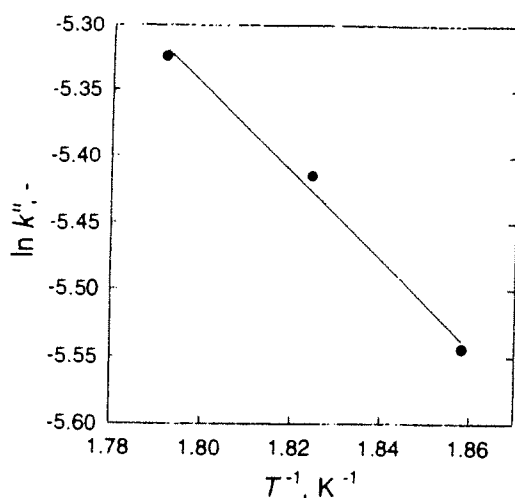


Figure 9 — Determination of Arrhenius parameters for the decarboxylation reaction in fusion synthesis of Ca-resinates.

The reaction rate constant for the decarboxylation reaction is smaller in the CO_2 -atmosphere ($k'' = 3.60 \times 10^{-3} \text{ (mol/kg)}^{-0.5} \text{ min}^{-1}$) than in the reference synthesis in the N_2 -atmosphere (Table 1), but the total amount of decarboxylated rosin is almost equal to the reference synthesis (Figure 6). Therefore, it is concluded that the decarboxylation reaction is also irreversible in a CO_2 -atmosphere.

Conclusions

The fusion synthesis of Ca-resinates takes place in two consecutive reaction steps, resination and decarboxylation reactions. To study these reactions FTIR analysis was successfully applied to determine the composition of the complex reaction media. Resination was observed to be a fast irreversible reaction step. After the resination reaction was completed the FTIR analysis of the resinate concentration increase enabled also calculation of the mass balance during the decarboxylation reaction.

A kinetic model proposed for the slow decarboxylation reaction step is based on the separate mechanisms for the free and solvating rosin acids. The model was tested with a demonstration system at three different reaction temperatures and the rate constants for the rosin acid decarboxylation were estimated. Comparison of the model predictions with actual experimental data (Figures 7 and 8) shows that the approach is useful and reliable to control the decarboxylation reaction.

Acknowledgement

The authors are grateful to Mr. Antti Ilves for help with the experimental work.

Nomenclature

c_i = concentration of compound i , (mol/kg)
 c_1 = resinate concentration at time t_1 , (mol/kg)
 c_2 = resinate concentration at time t_2 , (mol/kg)
 $c_{\text{RCOOH}(s)}$ = concentration of solvating rosin acids, (mol/kg)

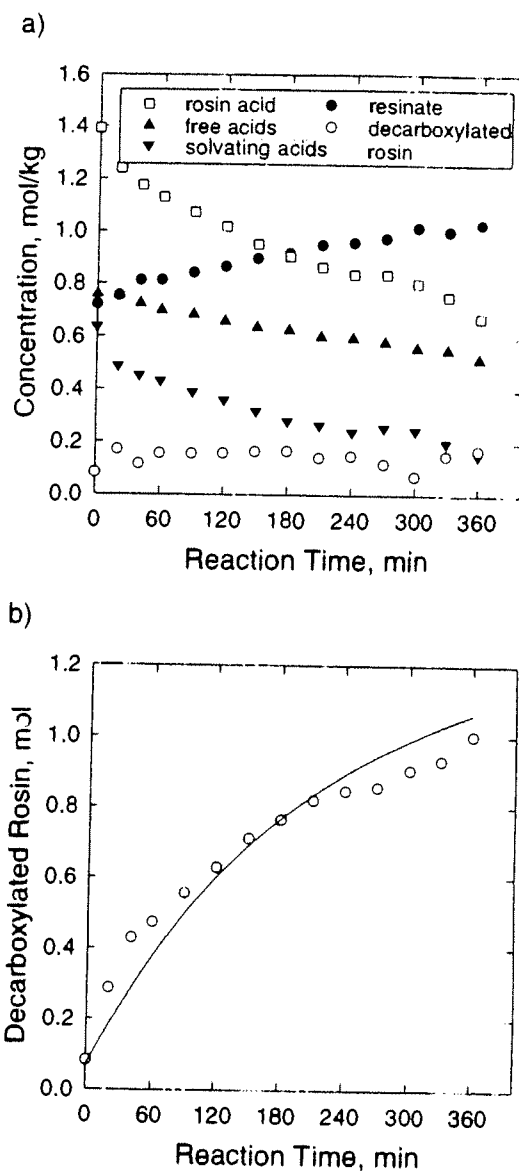


Figure 10 — Ca-resinate synthesis in CO_2 -atmosphere at 265°C . a) Concentrations in the reaction mixture; b) The amount of decarboxylated rosin and the fit of the kinetic model (reaction order 1.5).

$c_{\text{RCOOH}(f)}$ = concentration of free rosin acids, (mol/kg)
 k' = rate constant for the resination reaction, $((\text{mol/kg})^{-1} \cdot \text{min}^{-1})$
 k'' = rate constant for the decarboxylation reaction, $((\text{mol/kg})^{-0.5} \cdot \text{min}^{-1})$
 k_1 = rate constant for the decarboxylation of solvating rosin acids, $((\text{mol/kg}) \cdot \text{min}^{-1})$
 k_2 = rate constant for the decarboxylation of free rosin acids, $((\text{mol/kg})^{-1} \cdot \text{min}^{-1})$
 K_{ass} = equilibrium constant for the protolysis of free rosin acids

m_1 = mass of the reaction mixture at time t_1 , (kg)
 m_2 = mass of the reaction mixture at time t_2 , (kg)
 \dot{m}_v = vaporizing mass flow, (kg/min)
 n_i = amount of i in the reactor, (mol)
 $n_{i,v}$ = molar flow of i leaving the reactor by vaporizing, (mol/min)
 r_i = generation rate of compound i , ((mol/kg)^{1- α} ·min⁻¹)

Greek Symbols

α = reaction order
 Δm_{rel} = relative mass loss

Abbreviations

A = rosin acid group, RCOOH
 B = Ca(OH)₂
 R⁻ = carbanion intermediate

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III

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Application of IR spectroscopy and multivariate calibration to monitor the fusion synthesis of Ca- and Ca/Mg-resinates

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Abstract

The application of FTIR spectroscopy was studied in mid-infrared region (MIR) and near-infrared (NIR) region in fusion synthesis of Ca-resinates as well as Ca/Mg-resinates. Predictive calibration models based on partial least squares (PLS) regression were developed to describe the relationship between the spectra and the acid value of laboratory scale synthesized Ca-resinates. The relationship between the spectra and the viscosity of 50 wt% toluene solution of industrially processed Ca/Mg-resinates was also modelled with PLS. The results showed that both the calibration models can be applied to monitor the fusion resinate process. However, it was observed that pre-processing of the spectra with multiplicative scatter correction was necessary before the calibration. In acid value calibrations, linear PLS was sufficient for calibration, even when different rosin grades were used in the syntheses. For the solution viscosity calibrations, non-linear PLS had to be applied to obtain satisfactory calibration models. The models in the MIR and NIR regions were observed to be equally good for the calibration © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Ca/Mg-resinates; Fusion synthesis; PLS; FTIR; MIR; NIR

1. Introduction

Ca- and Ca/Mg-resinates are the salts of rosin acids (Fig. 1) and they are widely used as binders in publication gravure inks. Resinates are usually produced by the solution or the fusion method. In fusion synthesis of resinates the reaction steps include a fast irreversible resination reaction and a slow decarboxylation reaction of rosin acids forming neutral rosin oil. In addition, side reactions, isomerization and polymerization (mainly thermal dimerization) of rosin acids take place.

In the synthesis of Ca-resinates the progress of reactions is usually followed by acid value titration. The fusion resinate process is also followed by the solution viscosity measurements of the reaction media. The industrial scale resinate process is difficult to control because the solution viscosity increase is almost exponential after a specific reaction time [1]. Viscosity measurement of 50 wt% toluene solution of the resinate is time consuming and the acid value titration does not give enough information of the reaction system. Due to the relatively high reaction temperature (265°C), the application of direct in-line viscosity monitoring is technically difficult. Therefore, in this study an indirect monitoring system for resinate syntheses is introduced

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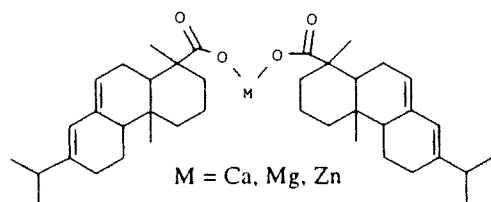


Fig. 1. Resinate molecule scheme.

and carried out based on the FTIR spectroscopic data.

In earlier studies of our group on resinsates [1], a semi-empirical two-parameter model for solution viscosity increase during the resinates synthesis was derived based on kinetic measurements of the acid value. The study includes the derivation of an empirical relationship between the viscosity (50 wt% resinates–toluene solution) and the rosin acid concentration in the reaction mixture. Later [2] this kinetic model was verified by the mechanistic study of the decarboxylation reaction of the rosin acids in the synthesis, where the resinates concentration was determined by FTIR using a conventional calibration method. The empirical viscosity model was developed for monitoring and prediction of the viscosity behaviour during the resinates process. However, in this study the multivariate approach based on FTIR analyses is carried out for easier monitoring of the kinetic and viscosity data by avoiding analytical and sampling problems of the complex resinates reaction mixture.

In the development of the kinetic model the concentrations of the chemical species of the reaction mixture are needed, especially at the initial stages of the reactions and at frequent intervals. It is also important to monitor and control the solution viscosity during the industrial scale resinates process. NIR spectrometer with an optical fibre probe can be used in-line and is, therefore, ideal for both the kinetic and process control applications, if the calibration problems typical for this technique can be solved.

Due to the considerable overlapping of the absorption bands in NIR region the classical calibration usually fails. The partial least squares (PLS) method has successfully been used in the calibration of multi-wavelength spectra [3–8]. The advantage of this method is that all the wavelengths can be included in the calibration. In MIR region this treatment of data

is also more informative than observing only one or two wavelengths of the spectrum.

For the acid value of the resinsates linear PLS [9] was used in calibration. Viscosity is a complicated function of the chemistry of the solution and, consequently, linear PLS did not give good results. However, in this case a sufficiently good calibration could be obtained by using non-linear PLS available in the PLS Toolbox by Barry Wise [10].

2. Experimental

2.1. Resinate syntheses

Ca-resinsates were synthesized by the fusion method in two different sizes of batch reactor vessels (300 and 1000 ml). The reaction mixture was stirred with a four blade impeller. Nitrogen was continuously bubbled through the reaction system. The syntheses were made from two different grades of tall oil rosin (acid values 164 and 175 mg(KOH)/g). Pro analysis quality $\text{Ca}(\text{OH})_2$ was used as the reactive metal salt and it was added in amounts of 6.0–7.5 wt% of rosin. The rosin was melted in the vessel at 235°C and the metal salts were gradually added to the rosin melt. After the resinates reaction was completed, the temperature was raised to the decarboxylation reaction temperature (265°C). The reaction time varied typically from 2.5–6 h depending on the amount of added metal salt.

2.2. Analyses

The acid value titrations of the resinates were carried out by the potentiometric titration of the acid concentration with 0.2 M KOH in toluene–ethanol solution with Mettler Toledo DL25 Titrator using the DG111-SC electrode.

A Perkin Elmer 2000 Infra-Red-Spectrophotometer equipped with a CaF_2 transmission cuvette (MIR/0.05 mm, NIR/1.0 mm) was used in the wavenumber region 9000–4000 cm^{-1} for NIR measurements and 4000–1000 cm^{-1} for MIR measurements. The sample was 15 wt% solution of the resinates. Toluene was used as a solvent in the MIR region and carbon tetrachloride in the NIR region.

The solution viscosities of industrially processed samples of fortified Ca/Mg-resinsates (50 wt% in

toluene) were measured at 20°C with a DIN 4 cup. It is a conventional way of measuring viscosity during the fusion resinate process.

3. Mathematical procedure

3.1. Pre-processing of MIR/NIR spectra

In MIR spectra (Fig. 2(a)) the specific absorption of Ca-resinate at 1560 cm⁻¹ increases with increasing reaction time and the absorption of dimeric forms of rosin acid (at 1694 cm⁻¹) decreases. In NIR spectra (Fig. 2(b)) the absorption over the whole spectrum increases with time, because of darkening of the samples as the reactions proceed.

The MIR/NIR spectra were pre-processed, if the calibration was improved, with the following methods to get the satisfying calibration. The spectra were used as the descriptor variables X in the calibration.

Moving median filter (MF) used as a data pre-processing technique was carried out to remove the sharp interference peaks occurring only in one or a few channels. An appropriate window for MF was observed to be seven for the NIR measurements. The first point in the filtered spectrum is the median of seven first points in the original spectrum. The second point is the median of the points from two to

eight in the original spectrum, etc. In the MIR spectra (Fig. 2(a)) a strong interference peak is observed at wavenumber about 1500 cm⁻¹. This peak was removed by median filtration using window number 25.

As the optical properties of the reaction mixture change during the course of the reaction this affects the calibration. Multiplicative scatter correction (MSC) [9] was used to increase the chemical information in the spectrum. MSC improved the results in almost all of the calibrations. In MSC, according to Eq. (1), the original spectra, $x_{ik,or}$, are regressed on the reference spectrum, $x_{ref,k}$, to get coefficients α_i and β_i and the residual term, $e_{ik,or}$. The average spectrum was used as the reference spectrum.

$$x_{ik,or} = \alpha_i + \beta_i x_{ref,k} + e_{ik,or}. \quad (1)$$

The MSC corrected data, x_{ik} , can be calculated from Eq. (2):

$$x_{ik} = (x_{ik,or} - \alpha_i) / \beta_i. \quad (2)$$

The spectra in Fig. 2 are median filtered and MSC corrected in Fig. 3.

Before PLS modelling the calibration set was centred. The test set was then centred with the mean of the calibration set. The wavenumber region 9000–7000 cm⁻¹ in the NIR region was left out to improve the calibration.

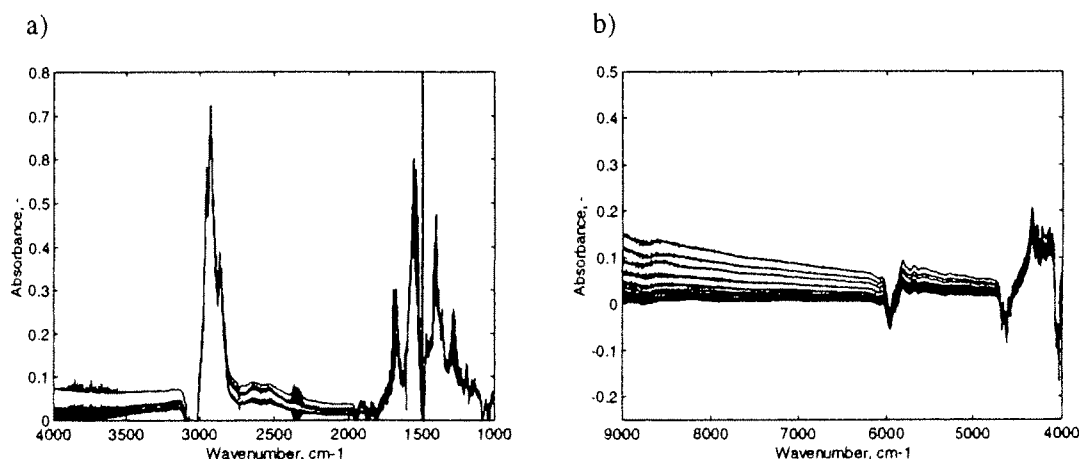


Fig. 2. FTIR spectra at different reaction times in the Ca-resinate synthesis by the fusion method: (a) MIR region; (b) NIR region.

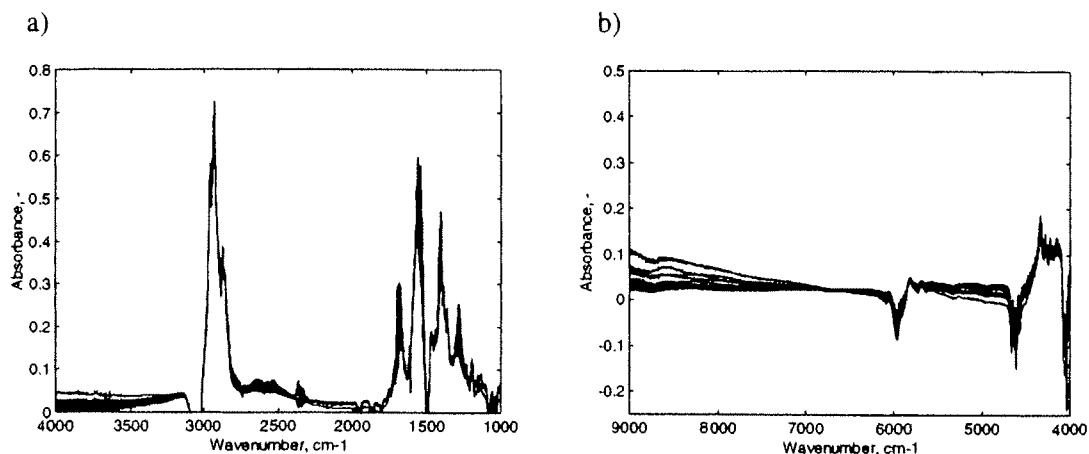


Fig. 3. Median filtered and MSC corrected FTIR spectra at different reaction times in the Ca-resinate synthesis by the fusion method: (a) MIR region; (b) NIR region.

3.2. Evaluation of the procedure

In the linear PLS method the number of latent variables, lv , for the descriptor variables was found by cross validation [9]. The procedure was performed by repeating the calibration I times (I is the number of the parts the analytical set was divided into) each time treating one I th part of the whole set as prediction objects and the rest of the data as calibration objects. In the end all the calibration objects had been treated as prediction objects. The predicted residual sum of squares, PRESS, was computed for the numbers of latent variables lv 1–6. The best estimates for lv values were those for which PRESS obtained a minimum.

The algorithm for the non-linear PLS used in this work can be found from Barry Wise's PLS toolbox in MATLAB [10,11]. In this non-linear PLS the relationship between the latent variables of the response and the descriptor variables is a polynomial of the degree n . One response variable y was used in the calibration at a time. The following procedure applying the bootstrap technique [12] was repeated 20 times to find the typical number of latent variables, lv , for the descriptor variables and the order n for the polynomial in the non-linear PLS model for each calibration. For the viscosity calibration 2/3 of the samples were randomly selected into the calibration set and 1/3 were left into the independent test set. The response variable was

scaled and centred and the descriptor variables were mean centred. The coefficients of determination for the modelling set, R^2 , and for the test set, Q^2 , were calculated according to Eqs. (3) and (4) for the number of latent variables lv 1–6 and the order n 1–8:

$$R^2 = 1 - \frac{\sum_i (y_{ic} - \hat{y}_{ic})^2 / n_c}{\sum_i (y_i - \bar{y}_i)^2 / (n_c + n_t)} \quad (3)$$

$$Q^2 = 1 - \frac{\sum_i (y_{it} - \hat{y}_{it})^2 / n_t}{\sum_i (y_i - \bar{y}_i)^2 / (n_c + n_t)} \quad (4)$$

where \hat{y}_{ic} and \hat{y}_{it} are the predictions in the test set and calibration set, and n_c and n_t are the number of observations in the calibration and test set, respectively. \bar{y}_i is the average of y_i .

The best estimates for lv and n values were those for which the coefficient of determination, Q^2 , obtained a maximum. The final calibration model was calculated by using the average of the best values of lv and n in the bootstrapping.

After the best estimates for lv in the linear model and lv and n in the non-linear model were found, the calibration was done by selecting some of the samples for the calibration set while the rest were left into the independent test set. The chemical analyses whose absolute values of the prediction errors ($|\hat{y}_{ic} - y_{ic}|$ or $|\hat{y}_{it} - y_{it}|$) were larger than three times the standard deviation of the prediction errors in the calibration or

the test sets, were considered as y outliers and were discarded.

The root mean square error of calibration (RMSEC) and the root mean square error of validation (RMSEV) between the measured and the predicted values were determined according to Eqs. (5) and (6):

$$\text{RMSEC} = \sqrt{\sum_i (y_{ic} - \hat{y}_{ic})^2 / n_c}, \quad (5)$$

$$\text{RMSEV} = \sqrt{\sum_i (y_{it} - \hat{y}_{it})^2 / n_t}. \quad (6)$$

4. Results and discussion

4.1. Calibration in MIR region

Acid value: The acid value was calibrated with the linear PLS model and the optimal number of latent variables was found to be three. The model set was the synthesis using 6.0 wt% $\text{Ca}(\text{OH})_2$ for 6 h reaction time and in the test synthesis 6.3 wt% $\text{Ca}(\text{OH})_2$ was used for 5 h. FTIR spectra were analysed in toluene. Fig. 4 shows the experimental and predicted acid values for the calibration and test sets. The calibration succeeded well, although slightly different amounts of $\text{Ca}(\text{OH})_2$ were used in the calibration and test syntheses.

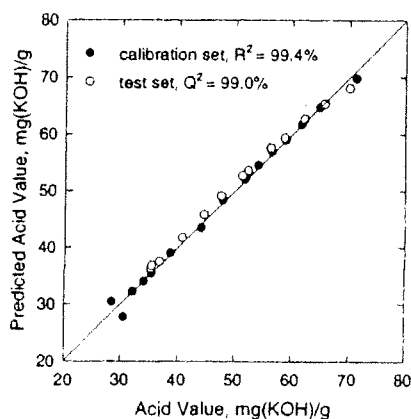


Fig. 4. Experimental and predicted acid values for the calibration and test sets in the Ca-resinate synthesis. MIR region, MSC corrected spectral data, linear calibration model ($lv=3$).

RMSEC for the calibration set and RMSEV for the test set were 1.0 and 1.5 mg(KOH)/g, respectively. The analytical error of the titration is considered to be smaller than 0.5 mg(KOH)/g.

Viscosity: The solution viscosity of 50 wt% toluene solution of the Ca/Mg-resinate was calibrated with non-linear PLS. The non-linear method was applied because of the critical concentration phenomenon [1] observed in resinate solution viscosity. The critical resinate concentration, in which the viscosity behaviour of the resinate solution considerably changes due to the increased molecular interactions, depends on resinate and rosin acid concentrations in the reaction mixture. In the calibration (Fig. 5), the number of latent variables was one and the order of the polynomial was three. The samples were from different batches of industrial scale resinate process at different reaction times. Every third observation was randomly included in the test set and the rest in the calibration set.

RMSEC for the calibration set was 2.0 s and for the test set RMSEV was 6.3 s. The analytical error for the viscosity measurement of 50 wt% toluene solution of resinate with a DIN4 cup is considered to be 0.5 s in low viscosity region (<25 s) and 1–3 s in high viscosity region (25–60 s) due to the high correlation between the viscosity and resinate concentration in the critical concentration region [1]. The strong deviation

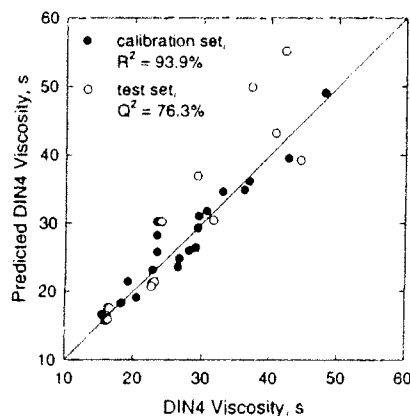


Fig. 5. Experimental and predicted solution viscosities for the calibration and test sets for the industrially processed Ca/Mg-resinate samples at different reaction times. MIR region, MSC corrected spectral data, non-linear calibration model ($lv=1$, $n=3$).

tions in measured and predicted values of high viscosity resins can be explained by the inaccuracy of the analytical measurement. The number of observations was rather low for the calibration, but it was concluded that it is possible to calibrate the solution viscosities from the MIR data. The calibration model is applicable for the monitoring of the resinate process, because a viscosity range for the product is as wide as 25–60 s. However, in process monitoring the viscosity measurements should be carried out near the highest and the lowest limit values to ensure that the product is in the required viscosity range.

4.2. Calibration in NIR region

Acid value: The acid value was calibrated with linear PLS and the number of the latent variables was three. The effect of different grades of rosin acids was studied: Rosin A with acid value 164 mg(KOH)/g and Rosin B with acid value 175 mg(KOH)/g. Every third observation was randomly selected in the test set and the rest in the calibration set (Fig. 6).

In addition the calibration was done for the combined set of Rosins A and B by randomly selecting every third observation to the test set and the rest to the calibration set (Fig. 7(a)). In Fig. 7(b) the calibration

Table 1

RMSEV and RMSEC between the measured and predicted acid values. Rosin A and Rosin B were used in the different syntheses of Ca-resinates

Model	RMSEV mg(KOH)/g	RMSEC mg(KOH)/g
Rosin A	1.7	1.1
Rosin B	2.6	2.1
Rosin A+Rosin B	6.7 (A)	2.3 (B)
Rosin AB (combined set)	2.5	2.5

was done from the synthesis using Rosin B, while the test set was from the synthesis using Rosin A.

The calibration succeeded when combining the sets of Rosins A and B for the total model (Fig. 7(a)). In Fig. 7(b) using different rosin grades in model and test sets, the calibration also succeeded in the model set acid value range, but the extrapolation to the acid values smaller than 35 mg(KOH)/g failed. RMSEC and RMSEV values were calculated for the different calibration and test sets (Table 1) using Rosins A and B. It is concluded that the different grades of tall oil rosin can be used when the calibration is made with the same range of acid values as in the test synthesis.

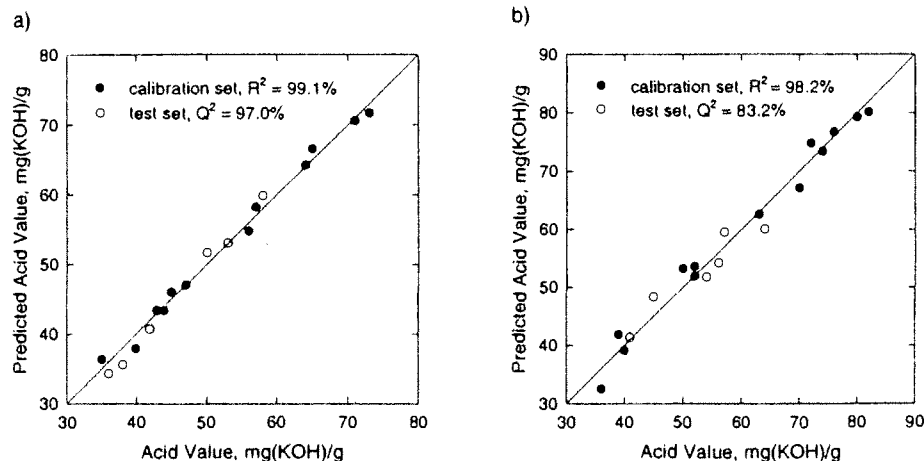


Fig. 6. Experimental and predicted acid values for the calibration and test sets in the Ca-resinate synthesis. NIR region, linear calibration model ($n=3$): (a) synthesis using Rosin A; (b) synthesis using Rosin B.

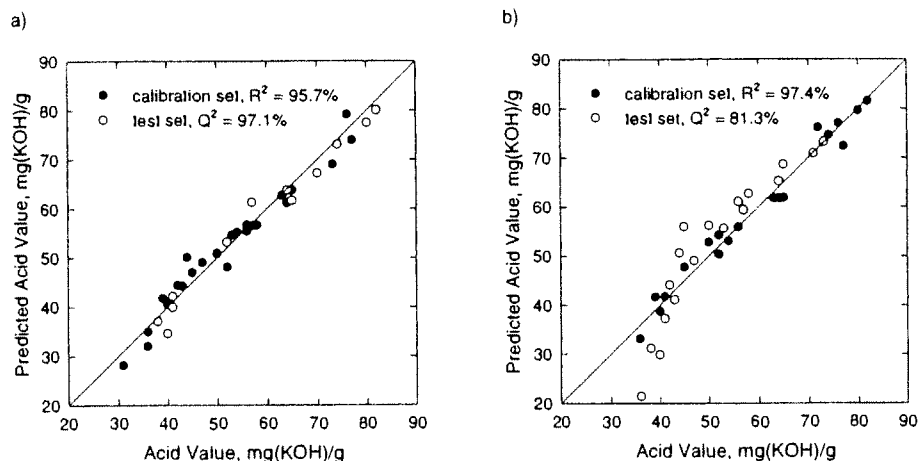


Fig. 7. Experimental and predicted acid values for the calibration and test sets in the Ca-resinate syntheses using Rosin A and Rosin B. NIR region, linear calibration model ($\nu=3$): (a) randomly selected calibration and test sets; (b) calibration set: synthesis using Rosin B; test set: synthesis using Rosin A.

Viscosity: The solution viscosity of the resinate was calibrated with non-linear PLS (Fig. 8), where the number of latent variables was three and the order of the polynomial was two. The samples

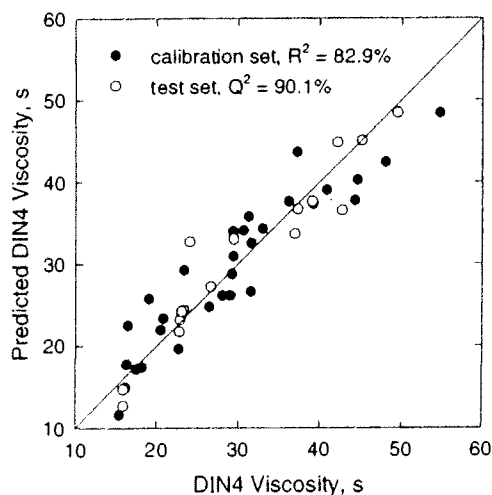


Fig. 8. Experimental and predicted solution viscosities for the calibration and test sets for the industrially processed Ca/Mg-resinate samples at different reaction times. NIR region, MSC corrected spectral data, non-linear calibration model ($\nu=3$, $n=4$).

were taken at different reaction times from batches of industrial scale resinate process. Every third observation was randomly included in the test set and the rest in the calibration set. RMSEC for the calibration set was 3.8 s and for the test set RMSEC was 3.2 s corresponding to the values of the calibration from the MIR spectra (Fig. 5) with fewer observations.

5. Conclusions

It was demonstrated in this study that Ca- and Mg-resinate syntheses can be monitored by IR spectroscopy combined with multivariate calibration methods. However, the spectra require to be preprocessed with multiplicative scatter correction before the calibrations. The acid value calibration models for Ca-resinate syntheses are successfully obtained in both the MIR and NIR regions with linear PLS regression. When the non-linear PLS is applied to calibrate the 50 wt% toluene solution viscosity of the industrially processed Ca/Mg-resinate samples, satisfactory calibration models are also obtained for both the MIR and NIR regions. However, NIR technique offers more options for process instrumentation due to the easier application of fibre optic probes.

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IV

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Decarboxylation of Rosin Acids in Fusion Synthesis of Ca-resinates — Thermogravimetric Studies

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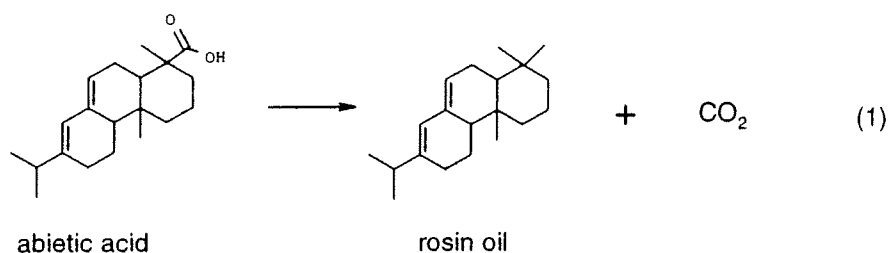
Abstract

Fusion synthesis of Ca-resinates was studied in a laboratory reactor and in a thermobalance. In the syntheses the resination reaction takes place at 235 °C and it is followed by the thermal decarboxylation of rosin acids at 265 °C. The kinetics of the thermal decarboxylation was modelled in the synthesis reactor using calcium contents corresponding to the theoretical target acid values 50 - 90 mg(KOH)/g, and in the thermobalance using different reaction temperatures (245 - 275 °C). The oxidative and thermal decarboxylation were separately studied in the thermobalance in different atmospheres (air, N₂, CO₂) at 260 °C. The oxidative decarboxylation was observed to be faster than the thermal decarboxylation during the first two hours. After that, however, the oxidative decarboxylation was restricted by the apparent reaction equilibrium.

Key words: *resinate, rosin acid, decarboxylation, thermobalance*

Introduction

The decarboxylation reaction of rosin acids is an essential reaction step in fusion syntheses of Ca-resinates. Resinates are metal salts of rosin acids, and they are used as binders in publication gravure inks. The physical properties of resinates, especially solution viscosity, are important when the resinates are used for printing purposes. The decarboxylation reaction, Equation (1), has been regarded as an undesired side reaction in the fusion synthesis (Oldring and Hayward, 1987) because it lowers mass yield of the synthesis as decarboxylated rosin (rosin oil) evaporates from the system. However, in our recent study (Sundqvist *et al.*, 1999) the importance of this reaction step in increasing resinate concentration of the reaction mixture has been pointed out. Direct resination reaction of unmodified rosin does not allow to control the solution viscosity increase to the desired level for the resinate to be used as an ink vehicle.



The decarboxylation of rosin acids is either a thermal or an oxidative reaction. Rosin acid decarboxylation has been studied at different temperatures (300 - 360 °C), by Wideman and Kuczkowski (1985), and in different atmospheres, by Szogalski and Mitskevich (1983, 1987). Szogalski and Mitskevich report greater amounts of decarboxylated acids in an air atmosphere than in a nitrogen atmosphere. This is due to the oxidation of the rosin acids by air. In an inert nitrogen atmosphere only thermal decarboxylation can occur and the rate of decarboxylation depends on temperature. The oxidative and thermal decarboxylation reactions are very important and need to be considered in the manufacturing and storing of resinates.

In our previous study (Sundqvist *et al.*, 1999) on fusion resinate synthesis in a nitrogen atmosphere, two main reaction steps were observed. A fast irreversible resination reaction occurs at 235 °C, and in the next reaction stage (at 265 °C) a slow thermal decarboxylation of rosin acids takes place. A semi-empirical kinetic model was first derived to facilitate the control of the non-linear viscosity increase during the fusion resinate syntheses (Sundqvist *et al.*, 1998). The viscosity model was then adjusted by studying the mechanism of the thermal decarboxylation reaction of rosin acids. The mechanistic model was based on the observation

that resinate molecules are partly solvated by free rosin acids during the syntheses. Therefore, different decarboxylation mechanisms were proposed for free and solvating rosin acids (Sundqvist *et al.*, 1999).

The previously derived kinetic model was limited to the calcium content of the product corresponding to a theoretical target acid value 70 mg(KOH)/g. In this study, the syntheses are carried out with different initial amounts of $\text{Ca}(\text{OH})_2$ to verify the previously derived mechanistic model for rosin acid decarboxylation. The kinetics of rosin acid decarboxylation at different reaction temperatures and in different atmospheres is investigated by thermogravimetric (TG) measurements. TG is used in order to obtain independent information and to avoid the difficult sampling and uncertainty in analysing the complex reaction media in fusion resinate synthesis.

Experimental

SYNTHESIS PROCEDURE

The same experimental setup as in our previous study (Sundqvist *et al.*, 1999) was used for the Ca-resinate syntheses. The syntheses were carried out in a 300 ml glass reactor and the reaction mixture was stirred with a four blade impeller. The temperature was controlled with an electrical muff. The system was purged with a constant nitrogen flow to apply an inert atmosphere. The raw material in the resinate syntheses was rosin with an acid value of 163 mg(KOH)/g, and a softening point of 63 °C. The composition of the rosin was ca. 81% rosin acids and 7% fatty acids. Calcium hydroxide (Riedel-deHaën, 95%) was used as a reactive metal salt.

In the syntheses, rosin was melted in the reactor, and $\text{Ca}(\text{OH})_2$ was gradually added at 235 °C. The amount of $\text{Ca}(\text{OH})_2$ added was equal to the amount required to obtain theoretical target acid values 50, 70 and 90 mg(KOH)/g for the product. After the salt addition, the temperature was increased to the decarboxylation reaction temperature (265 °C), and the reaction time was five hours.

ANALYTICAL METHODS

The reaction steps in the syntheses, resination and decarboxylation were followed by acid value titration and FTIR analyses.

Acid values of the resinates were determined by potentiometric titration with a Mettler Toledo DL25 Titrator using a DG111-SC electrode. The resinate sample was dissolved into a toluene–ethanol mixture and titrated with 0.2 M potassium hydroxide.

The resinate concentration increase and the concentration of the free rosin acids capable of associating to dimers in toluene were studied with a Perkin Elmer 2000 Infrared-Spectrophotometer. A CaF₂-cuvette (0.05 mm) was used and the sample was 15 w-% resinate-toluene solution. Calibration curves for the FTIR measurement of the complex resinate reaction media have been introduced in our previous study (Sundqvist *et al.*, 1999).

THERMOGRAVIMETRY

The decarboxylation reaction of rosin acids during the resinate syntheses was also followed in a thermobalance. In resinate syntheses the mass loss is due to the evaporation of neutral rosin oil and carbon dioxide, which are formed during the decarboxylation reaction, Equation (1). Therefore, the decarboxylation can be studied by measuring the mass loss by thermogravimetric (TG) analyses. TG studies were used to demonstrate the effect of temperature and different atmospheres on the decarboxylation reaction.

The measurements were carried out in a Netzsch STA 409 thermal analysis apparatus in nitrogen atmosphere at different temperatures (245 - 275 °C) for six hours. In addition, the effects of air atmosphere and carbon dioxide atmosphere on decarboxylation were studied at 260 °C. The resinate samples for TG measurements of decarboxylation reaction were taken from the syntheses after the resination reaction was complete and the temperature had been raised to 265 °C, at the decarboxylation reaction time $t = 0$. In TG measurements, because of the initial heating of the sample to reach the constant temperature, the first 20 - 35 minutes (depending on the final temperature) were not included in the kinetic study.

Kinetic model for decarboxylation

MECHANISTIC MODEL

The deduced mechanism for the rosin acid decarboxylation in the reaction mixture is based on the different reaction steps of solvating and free rosin acids analysed by FTIR. The mechanism is described in more detail in our previous study (Sundqvist *et al.*, 1999).

The protolysis equilibrium of the ion pair formation is considered for the free rosin acids. By applying the quasi-equilibrium approximation for the ion pair formation and assuming that the solvating rosin acids decarboxylate according to first order kinetics, with respect to the rosin acids, the total decarboxylation rate of rosin acids becomes:

$$r = k_1 c_{\text{RCOOH(s)}} + k_2 K_{\text{ass}} c_{\text{RCOOH(f)}}^2 \quad (2)$$

where k_1 and k_2 denote the decarboxylation rate constants for the solvating forms of rosin acids, RCOOH(s) , and for the free acids, RCOOH(f) , respectively. K_{ass} is the equilibrium constant of the ion pair association.

The reaction rate parameters are estimated separately based on the partial reaction rate equations (3) for the solvating and the free rosin acids ($i = \text{RCOOH(s)}$, RCOOH(f)). The overall rate equation (4) for decarboxylation is presented by means of partial reaction kinetics of the parallel reactions.

$$r_i = -\frac{1}{m} \frac{dn_i}{dt} = k_i c_i^{\alpha_i} \quad (3)$$

$$r_{\text{tot}} = r_{\text{RCOOH(s)}} + r_{\text{RCOOH(f)}} \quad (4)$$

If $r_{\text{RCOOH(s)}}$ and $r_{\text{RCOOH(f)}}$ are considered as being equal, the total reaction order for rosin acids becomes $\alpha_{\text{tot}} = 1.5$. The kinetic parameters were estimated from the differential equations (3) and (4) using the Simflex algorithm (Spendley *et al.*, 1962). The differential equations were solved by means of linear multistep methods implemented in ODESSA, which is based on LSODE software (Hindmarsh, 1983). The methods are available in the MODEST software (Haario, 1994).

MASS BALANCE CALCULATIONS

In fusion synthesis, the decarboxylation reaction of rosin acids takes place after the resination reaction is complete at 235 °C and the temperature is increased to the final reaction temperature (265 °C). Due to the vaporisation of the neutral rosin oil from the reaction system, the resinate concentration increases. In the experimental setup the rosin oil could not be collected and weighed quantitatively because it either solidified and blocked the distillation column or escaped through it.

The loss of mass during the decarboxylation reaction for six hours was measured as about 30 w-%. The mass balance of the syntheses is calculated by regarding the resinate amount as remaining constant (Sundqvist *et al.*, 1999). The increase in the resinate concentration indicates the relative mass loss of the system, and the loss can be calculated according to Equation (5) derived from the mass balance equation:

$$\Delta m_{\text{rel}} = 1 - m_2/m_1 = 1 - c_1/c_2 \quad (5)$$

where c_1 and c_2 denote the resinate concentrations in mol/kg, and m_1 and m_2 denote the masses of the reaction mixture at the reaction times t_1 and t_2 , respectively.

Results and discussion

DECARBOXYLATION IN A SYNTHESIS REACTOR

The syntheses were carried out with three different target acid values (50, 70 and 90 mg(KOH)/g) in order to extend the previously derived kinetic model for rosin acid decarboxylation to a wider resinate concentration region. The kinetic model has been derived using a theoretical target acid value 70 mg(KOH)/g (Sundqvist *et al.*, 1999) in a nitrogen atmosphere.

The reaction mixture compositions and mole amounts of the reactants are shown in Figure 1. The kinetic model, Equations (2)-(4), using parameter values $\alpha = 2.0$ for the free acids, $\alpha = 1.0$ for the solvating acids and $\alpha = 1.5$ for the total acids, is well fitted to the syntheses.

The results of the syntheses (Table 1) show that the best conversion of Ca(OH)_2 to resinate is obtained with the lowest metal amount (using target acid value 90 mg(KOH)/g). Also, the rate constant and the degree of decarboxylation are higher when the metal amounts are smaller in the syntheses. This is due to the higher number of free acid groups in the reaction mixture. The reaction rate constant of the reference synthesis (target acid value 70 mg(KOH)/g) is comparable to the value $4.56 \cdot 10^{-3} \text{ (mol/kg)}^{-0.5} \text{ min}^{-1}$ reported in our previous study (Sundqvist *et al.*, 1999).

TABLE 1

Effect of the amount of Ca(OH)_2 addition on the kinetic data of the syntheses.

Theoretical target acid value mg(KOH)/g	Conversion of Ca(OH)_2 to resinate mol-%	Degree of decarboxylation mol-%	Rate constant of decarboxylation $(\text{mol/kg})^{-0.5} \text{ min}^{-1}$
50	89.3	30.3	$3.33 \cdot 10^{-3}$
70	91.5	37.7	$4.79 \cdot 10^{-3}$
90	94.0	50.1	$5.40 \cdot 10^{-3}$

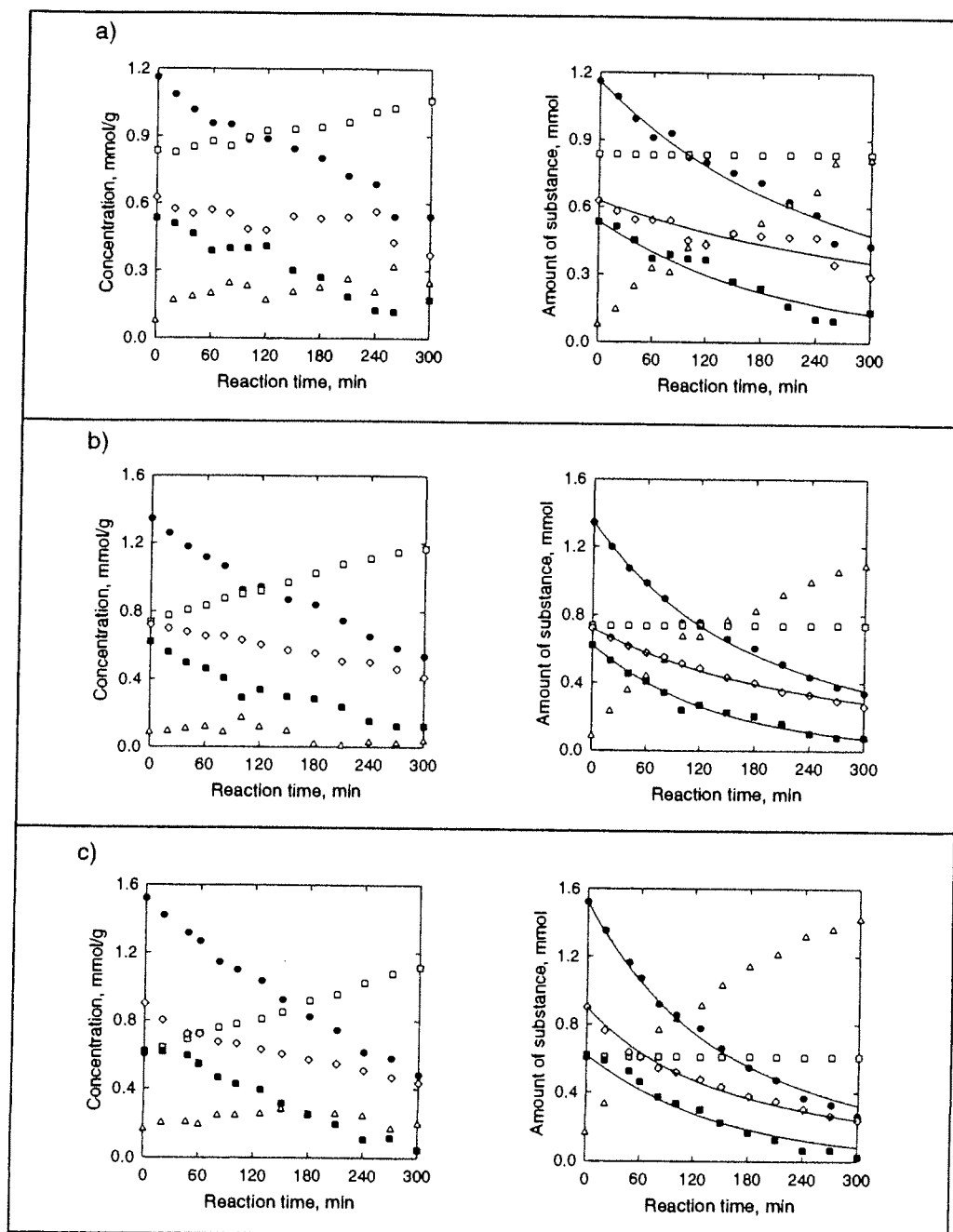


Figure 1 — Concentrations and amounts of the reactants in the fusion synthesis of Ca-resinates using different theoretical target acid values a) 50 b) 70 and c) 90 mg(KOH)/g. ● Total rosin acids, □ resinates, △ decarboxylated rosin, ◇ free rosin acids and ■ solvating rosin acids. The solid line is for the kinetic model with mass correction.

DECARBOXYLATION IN A THERMOBALANCE

In TG measurements, the rosin oil and carbon dioxide evaporate from the system during the decarboxylation reaction, Equation (1), and thus the amount of rosin acid in the sample can be calculated according to Equation (6):

$$n_{\text{RCOOH}}(t) = n_{0,\text{RCOOH}} - \frac{m_0 - m(t)}{M_{\text{CO}_2} + M_{\text{rosin oil}}} \quad (6)$$

where $n_{0,\text{RCOOH}}$ is the total amount of acid in the synthesis at the decarboxylation reaction time $t = 0$.

A comparison between the titrated acid content during the resinate syntheses and the amount of acid decrease measured by TG was done in order to apply the TG measurement to the kinetic study of the decarboxylation reaction. The rosin acid contents were calculated as mole amounts to demonstrate the decarboxylation reaction because the acid concentration change is greatly affected by the mass loss of the sample.

The acid value titration data from the synthesis for six hours reaction time was corrected with a mass balance calculation, and the rosin acid amounts of the TG sample were calculated relative to the initial mass of the synthesis. The synthesis results and the TG data are compared in Figure 2. Note, that the difference in the initial acid amounts ($t = 0$ h) is due to the heating of the TG sample to 265 °C. The figure demonstrates that TG measurements can be used as an efficient tool in the study of decarboxylation of resinate syntheses.

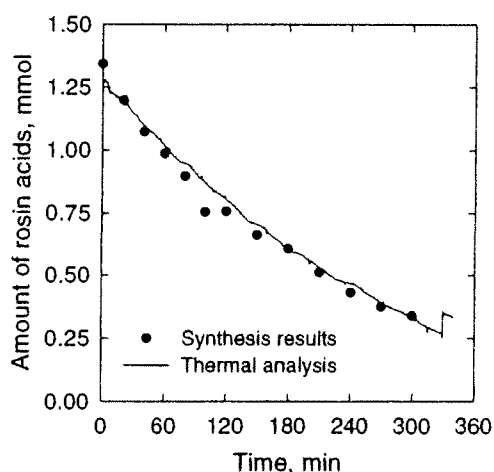


Figure 2 — Thermogravimetric data compared with the synthesis data in the decarboxylation studies of Ca-resinates.

Effect of atmosphere

TG measurements were carried out in nitrogen and air atmospheres in order to compare the thermal and oxidative decarboxylation reaction rates at 260 °C. The measurements were also carried out in a carbon dioxide atmosphere to study a possible equilibrium of the decarboxylation reaction, Equation (1). The samples were the rosin used as a raw material in the syntheses and the resinate from the reference synthesis (target acid value 70 mg(KOH)/g) at the decarboxylation reaction time $t = 0$.

It was observed that in the air atmosphere at 260 °C the decarboxylation of rosin (Figure 3) is in the beginning more rapid than thermal decarboxylation, but after five hours the oxidative reaction has reached the equilibrium state, while thermal decarboxylation still continues. Szogalski and Mitskevich (1987) have reported that the decarboxylated amount of rosin acids was about four times greater in an air atmosphere than in a nitrogen atmosphere at 240 °C due to the oxidative decarboxylation reaction. In their study, however, the equilibrium was not observed because of the short reaction time (60 min).

In Figure 3 it is also observed that no equilibrium is reached in a carbon dioxide atmosphere, and the decarboxylation follows the thermal decarboxylation curve of the reaction in a nitrogen atmosphere.

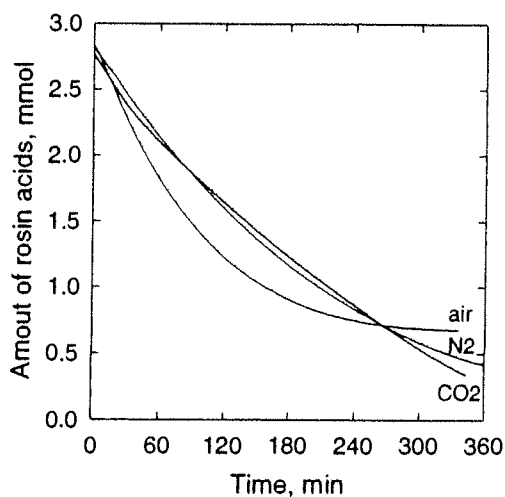


Figure 3 — Decarboxylation reaction of rosin in the thermobalance at 260 °C in different atmospheres. The rosin is used as a raw material in the fusion Ca-resinate syntheses.

In Figure 4a the rosin acids in the resinate reaction mixture reached the same equilibrium concentration of oxidative decarboxylation as pure rosin (Figure 4b) more rapidly. The equilibrium amount of rosin acids was 0.62 mmol, corresponding to the equilibrium concentration 0.81 mmol/g. It is anticipated that the apparent oxidative decarboxylation reaction equilibrium in the TG sample is affected by the mass transfer obstacle caused by the oxidative reaction products.

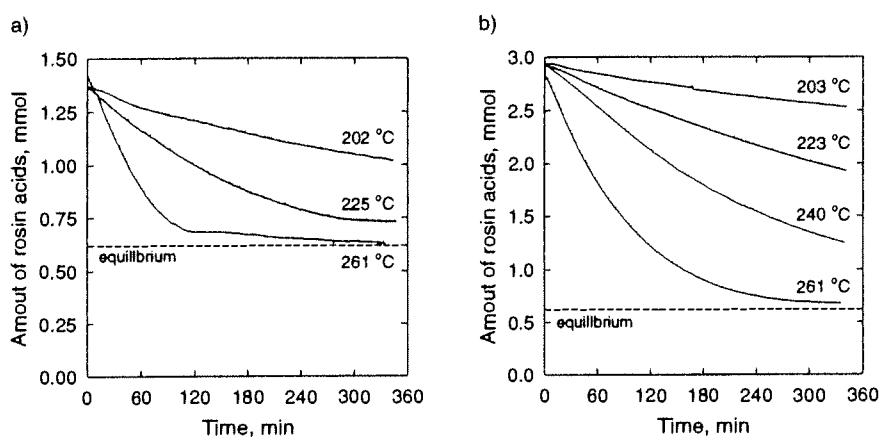


Figure 4 — Decarboxylation reaction in the thermobalance in an air atmosphere.
a) Resinate reaction mixture. b) Rosin used as a raw material in the fusion Ca-resinate syntheses.

Effect of temperature

The kinetic study of the thermal decarboxylation reaction was carried out in a thermobalance in a nitrogen atmosphere at different temperatures between 245 - 275 °C. The results of the syntheses (Figure 5) with different target acid values, i. e. different amounts of $\text{Ca}(\text{OH})_2$, followed well the change in total acid amount estimated by the kinetic model, Equation (4), with the parameter value $\alpha_{\text{tot}} = 1.5$.

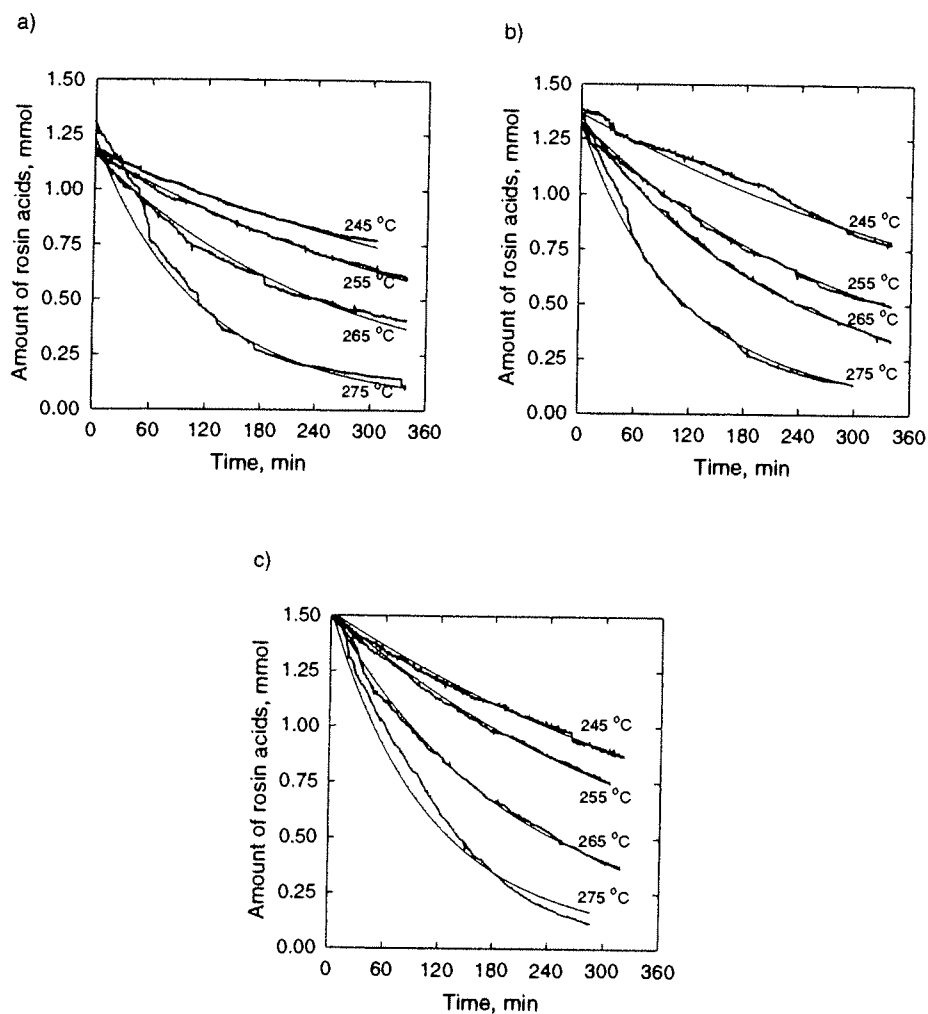


Figure 5 — Effect of reaction temperature on the decarboxylation reaction studied by TG in the fusion synthesis of Ca-resinates using different theoretical target acid values a) 50, b) 70 and c) 90 mg(KOH)/g. The continuous lines are for the kinetic model.

The distillation rate of rosin oil from the resinate in a thermobalance at 235 °C is shown in Figure 6. The rate is proportional to the added rosin oil, and with 0% addition only the neutral components of the raw material (rosin) evaporate. Because the kinetic model fits well to the data at different reaction temperatures (Figure 5) it is concluded that the distillation rate is proportional to the decarboxylation reaction rate depending on the reaction temperature. Thus the distillation rate is considered as being lumped into the kinetic model of decarboxylation.

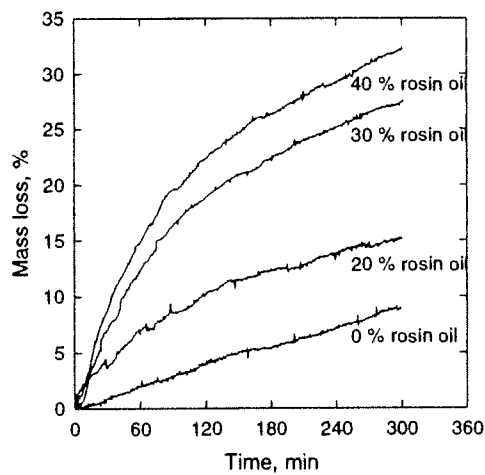


Figure 6 — Distillation of rosin oil in the thermobalance at 235 °C.

The activation energy of thermal decarboxylation of rosin acids was calculated according to the Arrhenius equation (7).

$$k(T) = A \cdot \exp[-E / (RT)] \quad (7)$$

The relationships between the rate constants and the temperatures are shown in Figure 7 for the syntheses using different theoretical acid values. The estimated reaction rate constants for the syntheses and the calculated activation energies are shown in Table 2.

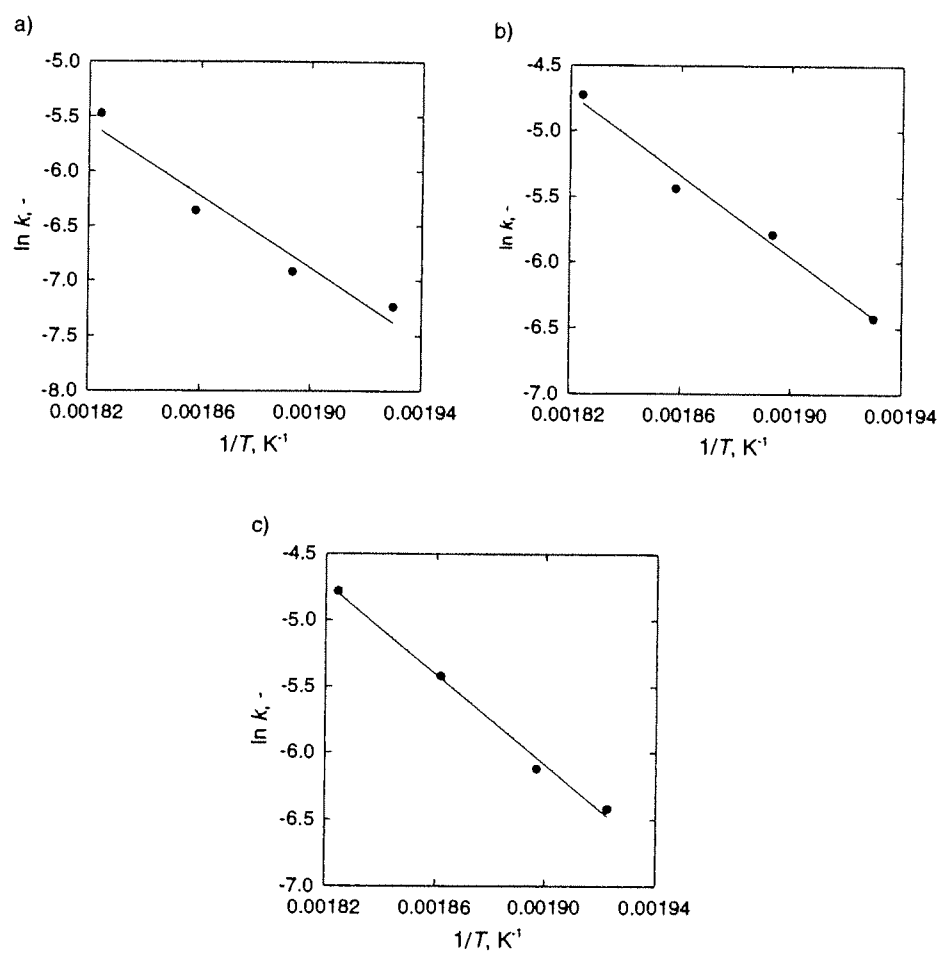


Figure 7 — Arrhenius plots for the fusion synthesis of Ca-resinates at 245-275 °C using different theoretical target acid values a) 50, b) 70 and c) 90 mg(KOH)/g.

TABLE 2

Thermal decarboxylation rate constants estimated by the kinetic model, Eq. (4), in fusion resinate syntheses at different reaction temperatures in a nitrogen atmosphere. Activation energies are calculated according to the Arrhenius equation, Eq. (7).

Theoretical target acid value mg(KOH)/g	Temperature °C	Rate constant (mol/kg) ^{-0.5} min ⁻¹	Activation energy kJ/mol
50	245	1.59 10 ⁻³	137.6
	255	2.19 10 ⁻³	
	265	3.83 10 ⁻³	
	275	9.29 10 ⁻³	
70	245	1.61 10 ⁻³	128.5
	255	3.06 10 ⁻³	
	265	4.32 10 ⁻³	
	275	8.82 10 ⁻³	
90	245	1.63 10 ⁻³	142.0
	255	2.19 10 ⁻³	
	265	4.41 10 ⁻³	
	275	8.33 10 ⁻³	

The results (Table 2) show that the activation energy for the thermal decarboxylation reaction is almost constant for the syntheses using different target acid values 50 - 90 mg(KOH)/g. In our previous study (Sundqvist *et al.*, 1999) we determined the activation energy 27 kJ/mol for the rosin acid decarboxylation in resinate syntheses at the temperature range 265 - 285 °C. The distillation rate of the rosin oil in the syntheses and in a thermobalance is proportional to the decarboxylation reaction rate and thus greatly affected by the temperature. The sensitivity of the determination of the activation energy explains the differences in the apparent activation energies at different temperature ranges.

Conclusions

The fusion Ca-resinate syntheses in this study verified that the previously derived mechanistic model for rosin acid decarboxylation is also valid when different metal amounts are used in the syntheses. The kinetic model was extended to a wider resinate concentration and thus to a wider viscosity region of the product than in the reference synthesis in which a theoretical target acid value 70 mg(KOH)/g was used.

The study also showed that the results of the decarboxylation kinetics obtained in the synthesis compare favourably with the thermogravimetric measurements. Therefore, TG was used to avoid difficulties in sampling and the analytical treatment of the complex reaction media. Based on the TG results, in the beginning of the reaction the thermal decarboxylation in the N₂- and CO₂-atmospheres is slower than the oxidative decarboxylation in the air atmosphere. However, the thermal decarboxylation still continues after the oxidative decarboxylation is restricted by the equilibrium state of the reaction.

The kinetic model of the decarboxylation applied to the TG studies at different reaction temperatures results in an almost constant value of the apparent activation energy in all the syntheses with different target acid values. The distillation rate of the rosin oil was observed to be proportional to the decarboxylation reaction rate and therefore considered as being lumped into the kinetic model. So, the value of the apparent activation energy includes the distillation rate of the rosin oil.

Nomenclature

- A = frequency factor in Eq. (7), $(\text{mol/kg})^{1-\alpha} \text{min}^{-1}$
 c_1 = resinate concentration at time t_1 , mol/kg
 c_2 = resinate concentration at time t_2 , mol/kg
 $c_{\text{RCOOH}(s)}$ = concentration of solvating rosin acids, mol/kg
 $c_{\text{RCOOH}(f)}$ = concentration of free rosin acids, mol/kg
 E = activation energy in Eq. (7), J/mol
 k_1 = rate constant for the decarboxylation of solvating rosin acids, $(\text{mol/kg}) \text{min}^{-1}$
 k_2 = rate constant for the decarboxylation of free rosin acids, $(\text{mol/kg})^{-1} \text{min}^{-1}$
 k = rate constant for the decarboxylation of total acids, $(\text{mol/kg})^{-0.5} \text{min}^{-1}$
 K_{ass} = equilibrium constant for the protolysis of free rosin acids, -
 m_0 = mass of the reaction mixture at time $t = 0$, kg
 $m(t)$ = mass of the reaction mixture at time t , kg
 m_1 = mass of the reaction mixture at time t_1 , kg
 m_2 = mass of the reaction mixture at time t_2 , kg
 M_i = molar mass of compound i , mol/kg
 n_{RCOOH} = amount of rosin acids, mol
 r_i = generation rate of compound i , $(\text{mol/kg})^{1-\alpha} \text{min}^{-1}$
 R = gas constant, $= 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
 T = temperature, K

Greek Symbols:

- α = reaction order, -
 Δm_{rel} = relative mass loss, -

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Modified Syntheses of Ca-resinates by Fusion Method

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Abstract — Tall oil rosin was modified with fumaric acid or maleic acid anhydride to get fortified rosin, which was used as a raw material in fusion Ca-resinate syntheses. Two reaction steps were observed in the syntheses. A fast resination reaction takes place at 235 °C and a slow decarboxylation of rosin acids forming neutral rosin oil at 265 °C. A mechanistic model for the decarboxylation reaction step was derived to explain the effect of fortifying substances on the reaction kinetics. A multivariate calibration method using partial least square regression (PLS) was applied in order to monitor the acid concentration decrease on the basis of infra-red spectroscopic data during the fortified syntheses.

A mixture of unmodified rosin and rosin oil (i. e. decarboxylated rosin) was used as a raw material in a novel modification of fusion syntheses to increase the mass yield of the resinate. In the rosin oil modified syntheses, decarboxylation of rosin acids is avoided and recycling the added rosin oil considerably improves the mass yield of the resinate syntheses.

Key words: *Ca-resinate, fortified rosin, decarboxylation, IR spectroscopy, PLS*

Introduction

Resinates are polyvalent metal salts of rosin acids. Ca- and Ca/Mg-resinates are used as binders in publication gravure inks and solution viscosity is an important quality specification of resinates to be used as an ink vehicle. In modified resinate syntheses, rosin is generally fortified by reacting it with a dienophile, such as maleic acid or maleic acid anhydride or fumaric acid. The reaction products are tricarboxylic acids which are referred to as maleopimaric or fumaropimaric acids. The rosin adducts have high melting points, and the acidity makes them reactive with metal hydroxides to form resinates with improved printing qualities.

In fusion resinate syntheses, a non-linear solution viscosity increase causes problems in monitoring and controlling of the resinate process. Direct resination reaction (Figure 1) is complete at 235 °C in a few minutes (Sundqvist *et al.*, 1999^b), but the reaction cannot be carried out to the desired viscosity level due to the blocking of the unreacted $\text{Ca}(\text{OH})_2$ as described by different authors (Petrone, 1971; Jilek, 1976; Oldring, 1987).

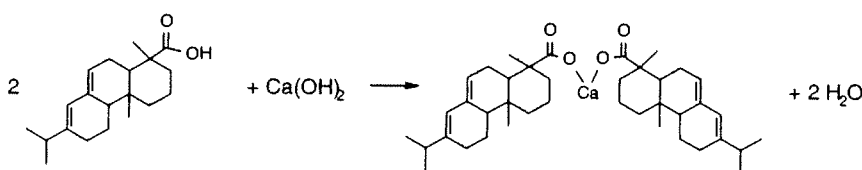


Figure 1. Resination reaction.

For this reason the viscosity is often raised to the required level at an increased reaction temperature (265 °C) to enable the thermal decarboxylation of rosin acids to take place. In the decarboxylation reaction step, volatile neutral rosin oil is formed (Figure 2). The rosin oil evaporates from the synthesis causing about 30% mass loss from the system. So, the resinate concentration in the reactor increases during the decarboxylation reaction step, and the target viscosity of the product can be obtained. However, such a loss of raw material (rosin) is undesirable for economic reasons.

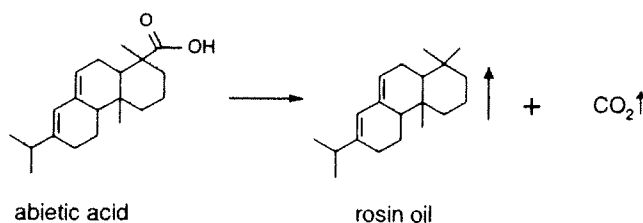


Figure 2. Decarboxylation reaction.

It is not easy to keep the non-linear viscosity increase under control without knowing the kinetics of the decarboxylation reaction. In our previous study (Sundqvist *et al.*, 1998) a semi-empirical viscosity model was derived to monitor and predict the solution viscosity increase during the fusion resinate process. The simplified kinetic model for the synthesis was deduced based on acid value measurements. Later (Sundqvist *et al.*, 1999^b) the kinetic model was verified by taking into account the mechanism of the thermal decarboxylation reaction. The reaction mechanistic studies were based on FTIR spectroscopic data analyses after having solved calibration problems of the complex reaction system. The mechanistic model was derived for the Ca-resinate synthesis using unmodified rosin as the raw material.

In fusion resinate synthesis, rosin modification is often done by using fumaric acid (FA) or maleic acid anhydride (MAA) as fortifying substances. The use of FA or MAA increases the rosin acid functionality (Figure 3) and therefore affects the mechanism of the resination reaction and the decarboxylation reaction. In the present study, the effect of rosin acid modifications on reaction kinetics is studied and a kinetic model for the decarboxylation in fortified syntheses is derived. FTIR analyses are carried out to measure the resinate concentration, free rosin acid concentration and the anhydride concentration of the complex reaction mixture. The total acid content is determined based on acid value titration, and thus the amount of rosin acids solvating the resinate molecules is calculated. The solvation phenomenon during resinate syntheses was observed in our previous study (Sundqvist *et al.*, 1999^b).

The multivariate calibration methods combined with IR analyses was previously applied (Sundqvist *et al.*, 1999^a) for the viscosity monitoring of the modified syntheses (industrial Ca/Mg-resinate samples). In this paper PLS calibration models are derived for the modified Ca-resinate syntheses using different amounts of FA and MAA in order to monitor the acid value during the syntheses.

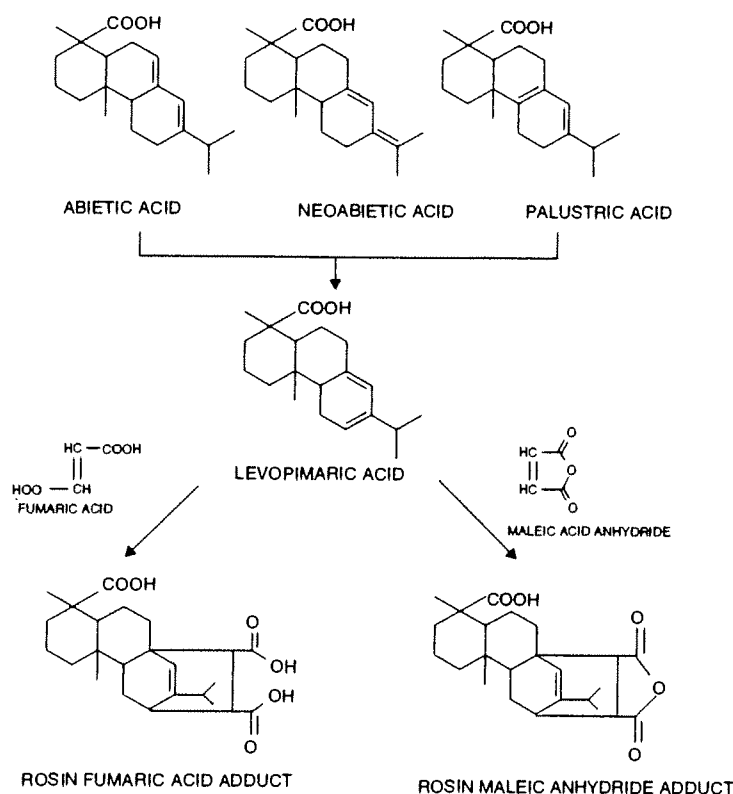


Figure 3. Fortification reactions of rosin acids.

In traditional fusion resinate syntheses at 265 °C, the target viscosity for the product is obtained during the decarboxylation reaction step. When decarboxylated rosin (i.e. rosin oil) evaporates from the system, the resinate concentration increases. Consequently, the mass yield of the synthesis decreases. In this study, however, in order to get improved mass yield, the resinate syntheses are carried out with rosin oil additions at 235 °C. The thermal decarboxylation is avoided by the lower reaction temperature. The addition of rosin oil to the reaction mixture enables further resination reaction with a higher degree of neutralisation of rosin acids than in traditional syntheses. Due to the higher resinate concentration in the reaction mixture, the solution viscosity of the resinates will increase to the desired level when the added rosin oil is evaporated. The mass yield of the rosin oil modified syntheses can be as high as 100% because of the possibility of recycling the added rosin oil in the reaction mixture.

Experimental

Fortified syntheses

The same experimental setup as in our previous study (Sundqvist *et al.*, 1999^b) was used for the Ca-resinate syntheses. The syntheses were carried out in a 300 ml glass reactor and the reaction mixture was stirred with a four blade impeller. The temperature was controlled with an electrical muff. The system was purged with a constant nitrogen flow to apply an inert atmosphere. The rosin (acid value = 163 mg(KOH)/g) used as a raw material in Ca-resinate synthesis was fortified by adding fumaric acid (FA) or maleic acid anhydride (MAA) into the rosin melt at 195 °C. The aliquots of the fortification substances were 2, 4 and 6 w-% of the rosin amount. The reaction time in fortifying the rosin was two hours.

After the fortification reaction the temperature was raised to 235 °C and Ca(OH)₂ was added into the reaction mixture. The Ca(OH)₂ addition was equal to the amount required to obtain the theoretical target acid value 70 mg(KOH)/g calculated for the resinate without fortification. After the resination reaction was complete (in about 15 minutes) the temperature was raised to the final reaction temperature (265 °C), and the reaction time was five hours.

Syntheses with rosin oil additions

In the syntheses with rosin oil additions, the mixture of rosin oil (acid value = 25 mg(KOH)/g) and rosin was heated to 235 °C. The rosin oil additions were 0, 20, 30 and 40 w-% of the rosin amount. The reaction time after Ca(OH)₂ addition was 30 minutes. The amount of salt addition was equal to the amount required to obtain the theoretical target acid values 0, 25, 50, 70 and 90 mg(KOH)/g calculated for the product.

Analyses

The complex reaction mixture was analysed by acid value titration and FTIR measurements. The potentiometric acid value titration was carried out with a Mettler Toledo DL25 Titrator using a DG111-SC electrode. The sample was diluted in toluene and an equal volume of technical alcohol was added into the solution. The titration was done using 0.2 M potassium hydroxide. In the potentiometric titration of fortified rosin and resinate, two equivalent points were recorded. In the first equivalent point, half of the anhydride is considered to be esterified by ethanol and the other half reacts with KOH (Zinkel *et al.*, 1989). Therefore, the acid concentration of fortified resinates was calculated based on the total consumption of the titer corrected by the titrated anhydride amount.

A Perkin Elmer 2000 Infra-Red-Spectrophotometer equipped with a CaF₂ transmission cuvette (0.05 mm) was used to measure the resinate concentration and the concentration of the free rosin acids capable of associating to dimers in toluene. The sample was 15 w-%

toluene solution of the resinate. The calibration for the FTIR analyses has been carried out in our previous study using abietic acid and Ca-abietate as standards (Sundqvist *et al.*, 1999^b). In addition, a new calibration was made using MAA fortified rosin as a standard for the anhydride concentration in the resinate reaction mixture.

Results and discussion

Fortified syntheses

Mass balance calculations

The effect of the fortifying substances on the composition of the resinate reaction mixture was studied. The mass balance of the fortified syntheses was calculated by regarding the resinate amount as constant after the resinification reaction has been complete and the temperature raised to 265 °C. Thus, the increase in the resinate concentration during decarboxylation indicates the relative mass loss of the system, and the loss can be calculated according to Eq. (1) derived from the mass balance equation:

$$\Delta m_{rel} = 1 - m_2/m_1 = 1 - c_1/c_2 \quad (1)$$

where c_1 and c_2 denote the resinate concentrations in mol/kg, and m_1 and m_2 denote the masses of the reaction mixture at the reaction times t_1 and t_2 , respectively. Based on mass balance calculations, which are discussed in more detail in our previous study (Sundqvist *et al.*, 1999^b), a decarboxylated amount of fortified rosin was calculated during the syntheses.

General progress of the syntheses

In the fortified resinate syntheses, it was observed that the amount of decarboxylated rosin acid is greater in fumaric acid modified resinate syntheses than in maleic acid anhydride modifications (Figure 4). This is partly explained by the greater amounts of acid groups in fumaric acid modifications. The average decarboxylation degree of rosin acids during the five hours' reaction time was 87% for FA modified syntheses and 78% for MAA modified syntheses. The value was 81% for the reference synthesis without fortification.

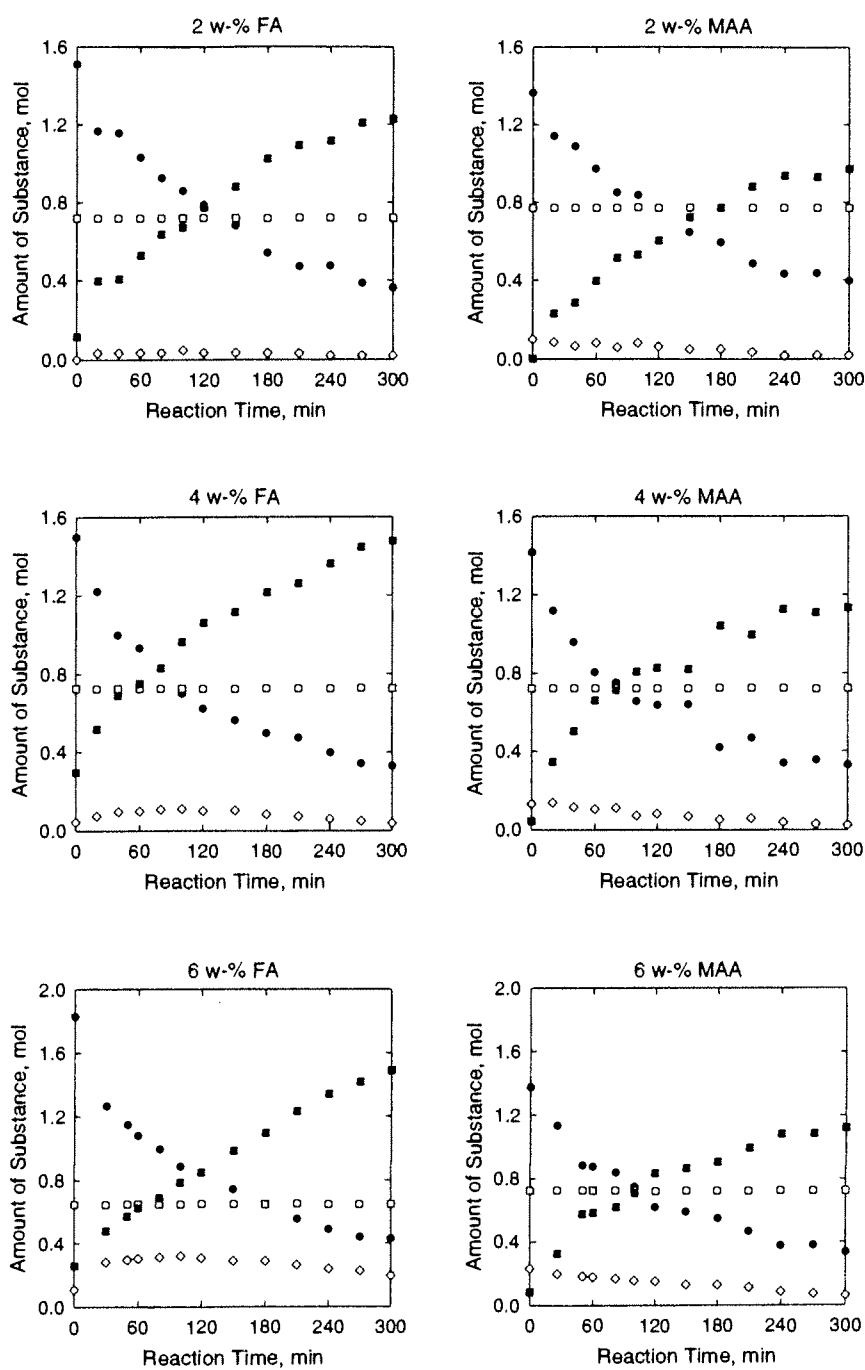


Figure 4. Mass corrected amount of substances in resinate syntheses modified with fumaric acid (FA) and maleic acid anhydride (MAA).

● Total acids, □ resinate, ◇ anhydride, ■ decarboxylated rosin.

Kinetic modelling of the decarboxylation

The previously published mechanism for the rosin acid decarboxylation in the reaction mixture is based on the different reaction steps of solvating and free rosin acids analysed by FTIR (Sundqvist *et al.*, 1999^b).

In the fortified resinate syntheses, the ratio between the free rosin acid concentration and the resinate concentration was compared to the same concentration ratio during unfortified reference synthesis. Figure 5 shows that the fortified rosin acids groups are free to associate to dimers in toluene solution analysed by FTIR.

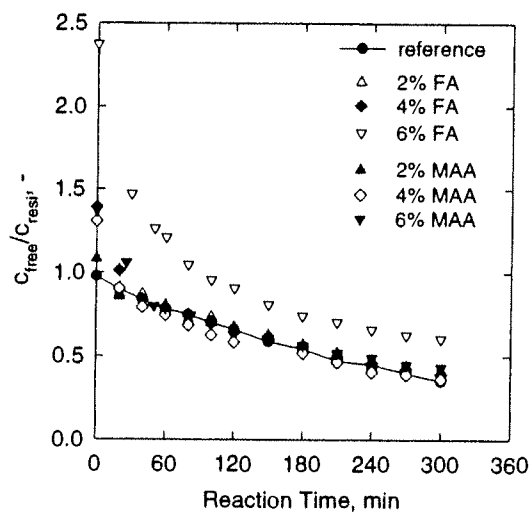
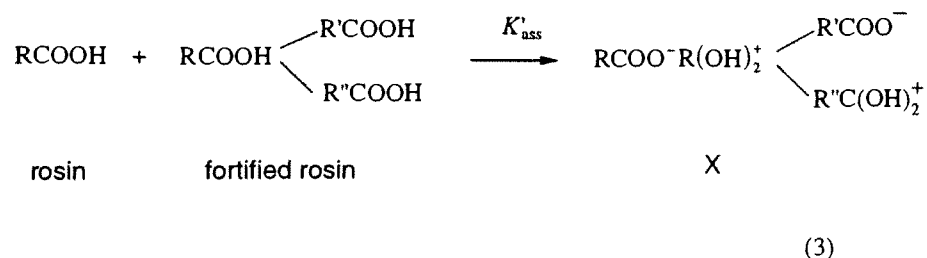


Figure 5. Ratio of free rosin acid concentration to resinate concentration in fortified resinate syntheses. The reference synthesis was carried out without fortification.

For the free rosin acids, RCOOH, the following protolysis equilibrium of the ion pair formation is considered:



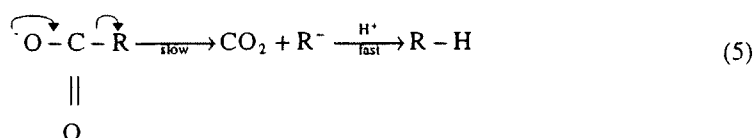
In the case of fortified rosin acids, the number of acid groups is three (Figure 3). Therefore, the assumed equilibrium for the free acids becomes:



The quasi-equilibrium approximation is applied to this rapid step (3) to express the concentration of the ion pairs X:

$$c_X = K'_{\text{ass}} c_{\text{RCOOH}}^4 \quad (4)$$

The decarboxylation of a carboxylate ion, RCOO^- , is generally believed to involve a carbanion intermediate (R^-) that subsequently acquires a proton from the solvent, or from another source (Sykes, 1986):



In the case of free rosin acid decarboxylation, the proton is available in ion pairs, and the delocalised structure of the solvating rosin acids is the proton source in the decarboxylation of solvating acids.

Loss of carbon dioxide is normally the rate limiting step and the subsequent proton abstraction is rapid (Sykes, 1986). So the rate law for decarboxylation becomes:

$$r_{\text{deca}} = k'' c_{\text{RCOO}^-} \quad (6)$$

By taking into account Eq. (4) and assuming that the solvating rosin acids decarboxylate according to first order kinetics, with respect to the rosin acid, the total decarboxylation rate of fortified rosin acids becomes:

$$r_{\text{deca}} = k_1 c_{\text{RCOOH(s)}} + k_2 K'_{\text{ass}} c_{\text{RCOOH(f)}}^4 \quad (7)$$

where k_1 and k_2 denote the decarboxylation rate constants for the solvating forms of the rosin acids, RCOOH(s) , and for the free acids, RCOOH(f) , respectively. K'_{ass} is the equilibrium constant of the ion pair association of fortified rosin.

The reaction rate parameters are estimated separately according to the partial reaction rate equations (8) for the solvating and the free rosin acids ($i = \text{RCOOH(s)}$, RCOOH(f)). The overall rate equation (9) for decarboxylation is presented by means of partial reaction kinetics.

$$r_i = -\frac{1}{m} \frac{dn_i}{dt} = k_i c_i^{\alpha_i} \quad (8)$$

$$r_{\text{deca}} = r_{\text{RCOOH(s)}} + r_{\text{RCOOH(f)}} \quad (9)$$

The kinetic parameters were estimated from the differential equation (8) using the Simflex algorithm, which is based on the simplex method introduced by Spendley *et al.*, 1962. The differential equations were solved by means of linear multistep methods implemented in ODESSA, which is based on the LSODE software (Hindmarsh, 1983). The methods are available in the MODEST software (Haario, 1994).

The best kinetic models are obtained, with the parameter values α and k , as shown in Table 1 and Table 2. The apparent reaction orders for total rosin acid decarboxylation depend on the amount of the fortifying substance used. Figure 6 shows that the kinetic model with the deduced reaction mechanism is well fitted to the analytical data.

Table 1. Reaction orders of the kinetic model, Eq. (8), in the fortified resinate syntheses.

Amount of FA/MAA w-%	Apparent reaction order, α		
	Total acids	Free acids	Solvating acids
2.0	1.5	4.0	1.0
4.0	2.0	4.0	1.0
6.0	2.5	4.0	1.0

Table 2. Reaction rate parameters for the total decarboxylation reaction and partial reactions for free acids and solvating acids in the fortified resinate syntheses.

Amount of FA/MAA w-%	Reaction rate parameter (mol/kg) ^{1-α} min ⁻¹		
	Total acids	Free acids	Solvating acids
FA 2.0	5.28 10 ⁻³	1.78 10 ⁻²	5.96 10 ⁻³
FA 4.0	6.48 10 ⁻³	1.82 10 ⁻²	7.98 10 ⁻³
FA 6.0	4.66 10 ⁻³	3.48 10 ⁻²	8.73 10 ⁻³
MAA 2.0	4.83 10 ⁻³	1.45 10 ⁻²	6.52 10 ⁻³
MAA 4.0	6.54 10 ⁻³	2.09 10 ⁻²	7.45 10 ⁻³
MAA 5.0	5.71 10 ⁻³	1.59 10 ⁻²	6.01 10 ⁻³

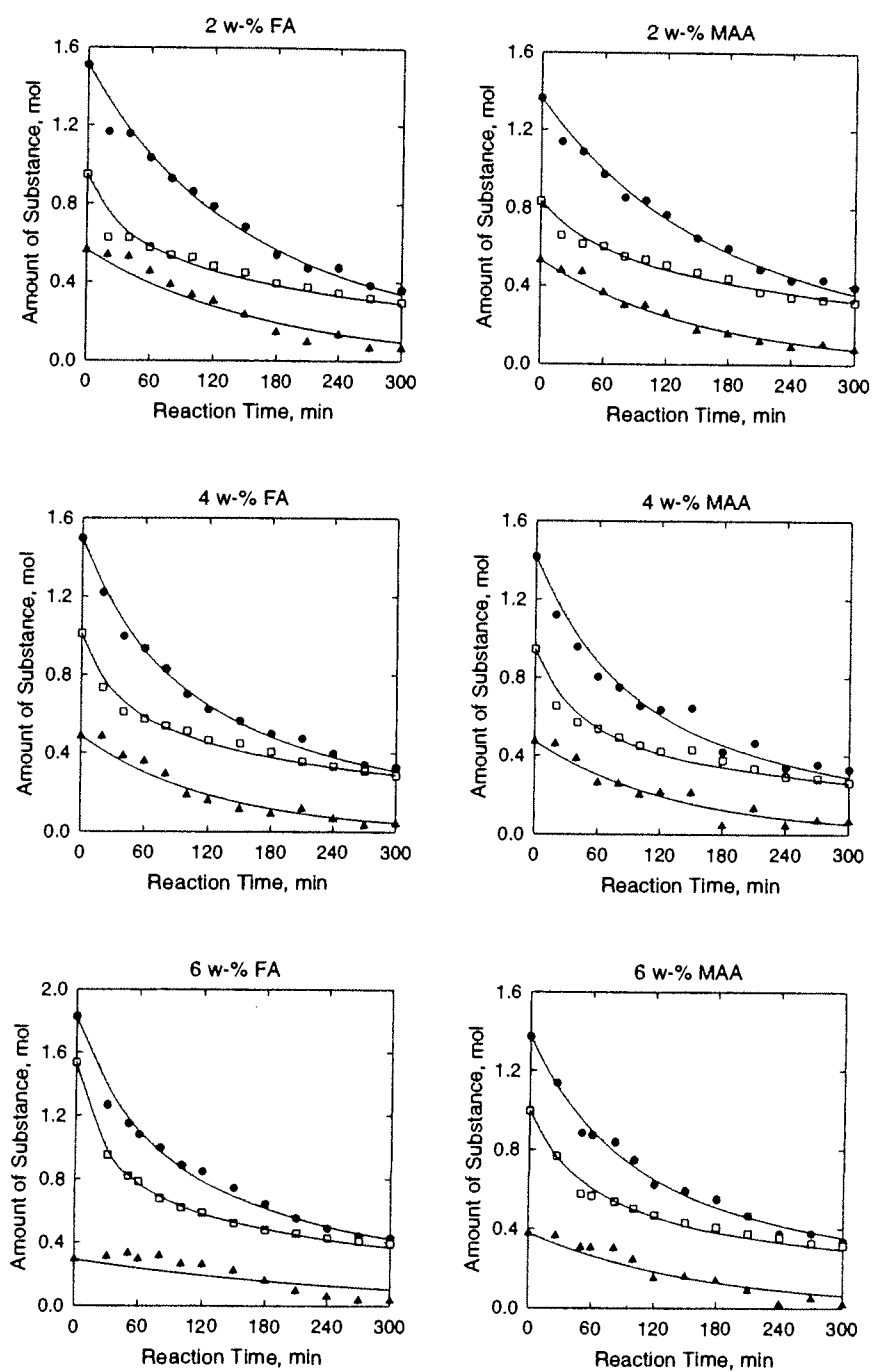


Figure 6. Application of the kinetic model, Eq. (8), to the decarboxylation reaction of the fortified rosin. ● Total acids, □ free acids and ▲ solvating acids.

PLS calibration models for acid concentration

Predictive calibration models based on partial least square regression (PLS) were developed to describe the relationship between the FTIR spectra and the acid concentration of FA and MAA fortified Ca-resinates. The spectra were used as the descriptor variables X in the calibration. Before PLS modelling, the calibration set was centred. The test set was then centred with the mean of the calibration set. The application of the PLS method has been discussed more in detail in the previous study in which the method was applied to unmodified resinate syntheses and to viscosity calibration of industrial fortified samples (Sundqvist *et al.*, 1999^a).

The acid concentration was calibrated with the linear PLS model. The optimal numbers of latent variables for different calibrations (Table 3) were found by cross validation (Martens and Næs, 1993).

Table 3. Optimal number of latent variables in the different calibrations of acid concentration in fortified Ca-resinate syntheses by the fusion method. The calibration is based on FTIR spectroscopic data.

Calibration set	Test set	Number of latent variables
4.0 w-% FA	I) 2.0 w-% FA	3
	II) 6.0 w-% FA	
4.0 w-% MAA	I) 2.0 w-% MAA	2
	II) 6.0 w-% MAA	
2/3 of FA data (randomised)	1/3 of FA data	4
2/3 of MAA data (randomised)	1/3 of MAA data	5

Figures 7 and 8 show the experimental and predicted acid values for the calibration and test sets. In Figure 7 the model set was the synthesis using 4.0 w-% fortifying substance and in the test sets the syntheses were with 2.0 w-% and 6.0 w-% additions. The calibration succeeded well in the 2.0 w-% FA modification and in MAA modifications.

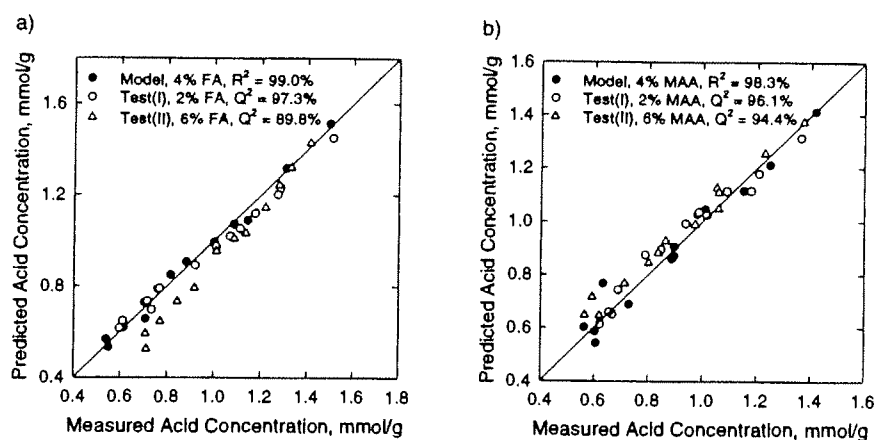


Figure 7. Measured and predicted acid concentrations in fortified Ca-resinate syntheses. Linear PLS calibration is based on FTIR spectroscopic data. Fortification with a) fumaric acid and b) maleic acid anhydride.

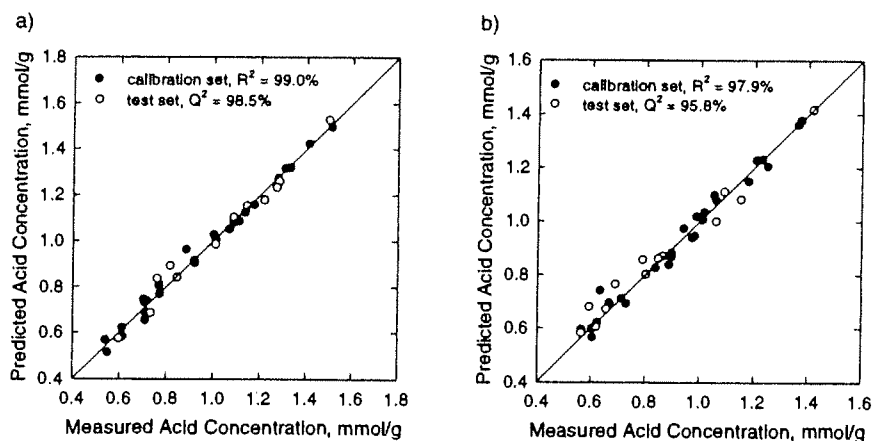


Figure 8. Measured and predicted acid concentrations in fortified Ca-resinate syntheses. Linear PLS calibration is based on FTIR spectroscopic data. The calibration and test sets are randomly selected from the data set. Fortification with 2, 4 and 6 w-% of a) fumaric acid and b) maleic acid anhydride.

In the calibration with randomised models (Figure 8), the calibrations were made for the FA and MAA fortified syntheses separately. Every third observation was randomly included in the test set and the other observations in the calibration set. The randomised calibration models were found to be better than using only one of the syntheses for calibration. Furthermore, the randomised models are applicable for monitoring of the resinate syntheses with different fortification degrees.

Syntheses with rosin oil addition

In traditional fusion syntheses of Ca-resinates it is difficult to control the solution viscosity increase and to obtain a product in the target viscosity region because of the non-linear solution viscosity increase during the decarboxylation reaction (Sundqvist, *et al.*, 1998). In the present study, rosin oil is added in order to obtain increased conversion of $\text{Ca}(\text{OH})_2$ to resinate at 235 °C and an increased degree of neutralisation of rosin acids. In this way the target viscosity level ($> 50 \text{ mPa s}$) for the resinate can be obtained without the decarboxylation reaction. Because rosin oil formation is avoided, the mass yield of the syntheses can be increased to a higher level (almost to 100%) than in traditional fusion synthesis (about 70 %), by evaporating and recycling the added rosin oil.

A derivation of an empirical correlation between the reaction mixture composition and solution viscosity is done in order to calculate the theoretical viscosity values for the resinate synthesised with rosin oil addition. The evaporation of rosin oil was studied in a thermobalance (Sundqvist *et al.*, submitted), and therefore the viscosity of the resinate sample after evaporation was not measured in the present study. The viscosity was calculated based on an empirical correlation between solution viscosity and the reaction mixture composition. The ratio of resinate concentration to the acid concentration was used to describe the composition of the relatively complex reaction mixture.

Effect of rosin oil addition/evaporation on resinate viscosity

The solution viscosity of resins has been observed to be highly dependent on the mass concentration of the resinate in toluene (Sundqvist *et al.*, 1998). A similar effect is observed when rosin oil is used as a solvent for the resinate (Figure 9). Therefore, it is necessary to evaporate all the added rosin oil from the reaction mixture, in order to obtain the target viscosity for the product.

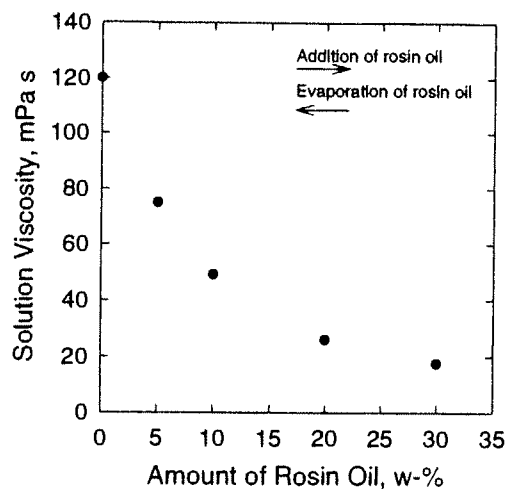


Figure 9. Effect of rosin oil addition on solution viscosity.

Effect of rosin oil addition on solvation

Rosin oil was used as a solvent for resinate in the syntheses. Thus the effect of the added rosin oil on the solvation of resinate molecules was studied with different amounts of rosin oil added in the syntheses (Figure 10). At low degrees of neutralisation (target acid values 70 and 90 mg(KOH)/g), the concentration ratio of free rosin acids to resinate increases with the increased rosin oil additions. This dilution effect is not so evident with the target acid values 0, 25 and 50 mg(KOH)/g, where the degree of neutralisation is high.

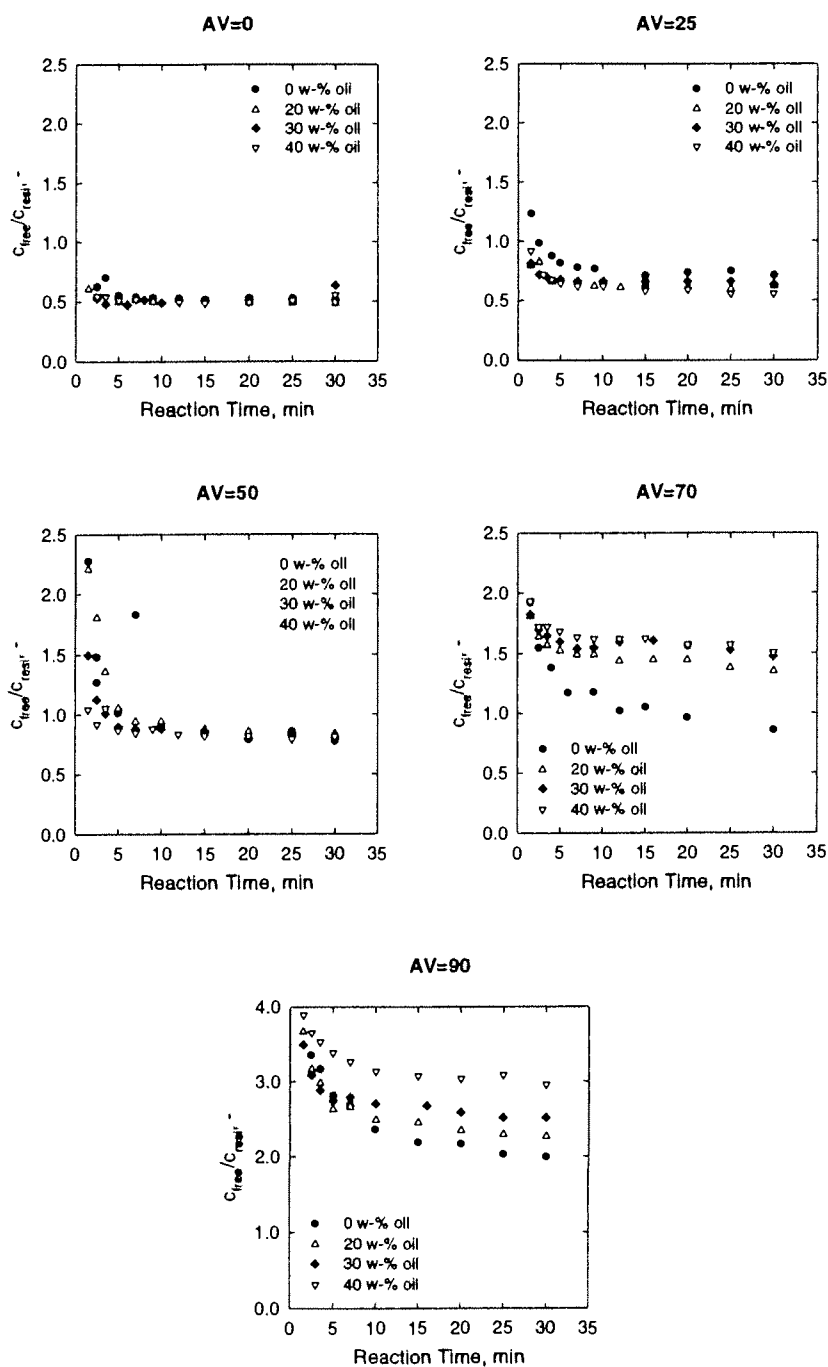


Figure 10. Ratio of free rosin acid concentration to resinate concentration with different theoretical target acid values (AV) used in the syntheses. Rosin oil additions are 0 - 40 w-%.

Effect of rosin oil addition on conversion

The high degree of neutralisation of rosin acids is required in order to obtain the target viscosity for the resinate. In traditional fusion syntheses, the decarboxylation of rosin acids forming neutral rosin oil results in a high degree of neutralisation. In the modified syntheses with rosin oil additions, the rosin acids can be highly neutralised through the increased conversion of $\text{Ca}(\text{OH})_2$ to resinate. Figure 11 indicates that the conversion of $\text{Ca}(\text{OH})_2$ to resinate depends on the theoretical target acid value (degree of neutralisation). Using target acid values 0 and 25 mg(KOH)/g, the conversion is significantly increased with rosin oil additions. When the degree of neutralisation is smaller (with target acid values 50, 70 and 90 mg(KOH)/g) the conversion is about 90% without rosin oil addition, and the effect of rosin oil on the conversion is not so clear.

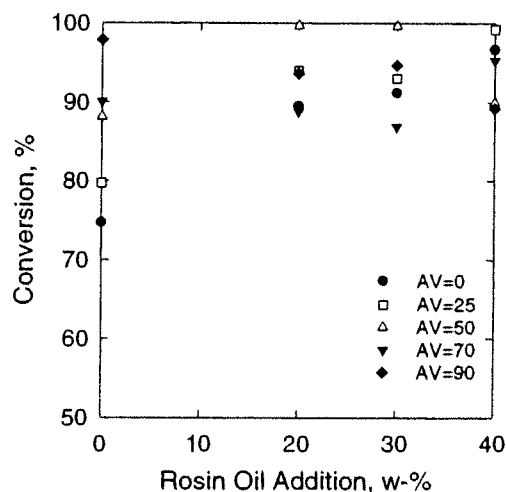


Figure 11. Effect of rosin oil addition on the conversions of $\text{Ca}(\text{OH})_2$ to resinate in the fusion syntheses with different theoretical target acid values (AV).

Calculation of theoretical viscosity values for the product

Solution viscosity of 50 w-% resinate–toluene solution is an important quality factor for resins to be used as an ink vehicle. An empirical correlation between the viscosity and acid concentration has previously been introduced in our study (Sundqvist *et al.*, 1998). However, in order to specify the empirical correlation between the viscosity and the chemical composition of the reaction mixture, the composition is described with the ratio of resinate concentration to the acid concentration (Figure 12) and the empirical correlation, Eq. (10), is thus obtained.

$$\frac{1}{\eta} = 0.02105 \left(\frac{c_{\text{resi}}}{c_{\text{acid}}} \right)^2 - 0.10568 \left(\frac{c_{\text{resi}}}{c_{\text{acid}}} \right) + 0.13490 \quad (10)$$

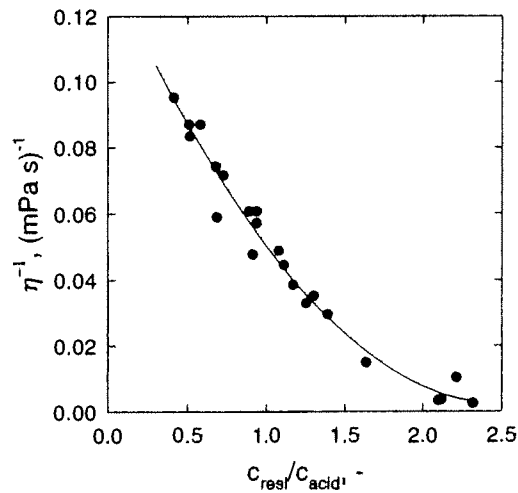


Figure 12. Empirical correlation between the viscosity of 50 w-% resinate–toluene solution and the composition of the reaction mixture described as the concentration ratio of resinate to rosin acids. The curve is calculated according to Eq. (10).

The theoretical viscosity values (Table 4) were calculated for the 50 w-% resinate–toluene solution according to Eq. (10). In the calculations, it was assumed that all the added rosin oil had been evaporated from the reaction mixture.

Table 4. Composition of the resinate with rosin oil addition. The viscosity values of 50 w-% resinate-toluene solutions are calculated according to Eq. (10) assuming that all the added rosin oil has been evaporated.

Target acid value mg(KOH)/g	Rosin oil addition w-%	Rosin acid concentration mmol/g	Resinate concentration mmol/g	$C_{\text{resi}}/C_{\text{acid}}$	Calculated viscosity mPa s
0	0	0.692	1.077	1.56	45.6
	20	0.660	1.008	1.53	43.4
	30	0.583	0.980	1.68	55.7
	40	0.476	0.982	2.06	122
25	0	0.925	1.005	1.09	23.1
	20	0.840	0.910	1.08	23.0
	30	0.797	0.855	1.07	22.7
	40	0.675	0.855	1.27	29.7
50	0	1.042	0.905	0.87	17.2
	20	1.002	0.823	0.82	16.2
	30	0.950	0.785	0.83	16.3
	40	1.023	0.635	0.62	12.6
70	0	1.327	0.765	0.58	12.0
	20	1.396	0.626	0.45	11.0
	30	1.377	0.539	0.39	11.1
	40	1.368	0.578	0.42	11.0
90	0	1.410	0.650	0.46	11.0
	20	1.537	0.514	0.33	-
	30	1.554	0.494	0.32	-
	40	1.886	0.460	0.24	-

As a conclusion, the resinate to be used in printing industry can be synthesised with the target viscosity value (> 50 mPa s) using theoretical target acid value 0 mg(KOH)/g and rosin oil additions 30 and 40 w-%. Then the target viscosity is obtained with a conversion of 90 - 95% $\text{Ca}(\text{OH})_2$ to resinate.

Conclusions

This study showed that the kinetics of fortified resinate syntheses using fumaric acid (FA) and maleic acid anhydride (MAA) as fortifying substances can be described by basically the same mechanistic model as previously derived for unmodified resinate syntheses. The acid groups in the fortified rosin are observed to be free acid groups capable of associating to dimers in toluene. The free acid groups of fortified rosin are observed to decarboxylate via ion pair formation resulting in an apparent reaction order of 4.0 for the free acids.

In the FA or MAA fortified resinate syntheses, multivariate calibration models using a linear PLS regression were applied to monitor the acid concentration decrease on the basis of FTIR spectroscopic data. Randomised calibration data, using different amounts of fortifying substances in the syntheses (2 - 6 w-%), gave useful models to be applied for process monitoring.

In addition, in this study a new modification of resinate synthesis, which includes rosin oil additions during the fusion synthesis, was introduced. The modified syntheses were carried out at a lower reaction temperature (235 °C) than in traditional fusion synthesis (265 °C). Therefore, the decarboxylation reaction was avoided during the syntheses. Using a stoichiometric amount of $\text{Ca}(\text{OH})_2$ to neutralise all the rosin acids, the conversion of $\text{Ca}(\text{OH})_2$ to resinate increased from 75% to 95%, when the rosin oil was added during the resination reaction step. The target viscosity of the resins is then obtained by evaporation of the added rosin oil. Recycling the rosin oil enables the mass yield to be increased from 70% to almost 100%.

Notation

c_i = concentration of compound i , mol/kg

c_1 = resinate concentration at time t_1 , mol/kg

c_2 = resinate concentration at time t_2 , mol/kg

$c_{\text{RCOOH}(s)}$ = concentration of solvating rosin acids, mol/kg

$c_{\text{RCOOH}(f)}$ = concentration of free rosin acids, mol/kg

c_x = concentration of ion pairs (Eq. 4), mol/kg

k'' = rate constant for the decarboxylation reaction, $(\text{mol/kg})^{1-\alpha} \text{min}^{-1}$

k_1 = rate constant for the decarboxylation of solvating rosin acids, $(\text{mol/kg}) \text{min}^{-1}$

k_2 = rate constant for the decarboxylation of free rosin acids, $(\text{mol/kg})^{-3} \text{min}^{-1}$

K_{ass} = equilibrium constant for the protolysis of free rosin acids, -

K'_{ass} = equilibrium constant for the protolysis of fortified rosin acids, -

m_1 = mass of the reaction mixture at time t_1 , kg

m_2 = mass of the reaction mixture at time t_2 , kg

n_i = amount of i in the reactor, mol

r_i = generation rate of compound i , $(\text{mol/kg})^{1-\alpha} \text{min}^{-1}$

Greek Symbols:

α = reaction order, -

Δm_{rel} = relative mass loss, -

Abbreviations:

AV = acid value

FA = fumaric acid

MAA = maleic acid anhydride

PLS = partial least square regression

R^\cdot = carbanion intermediate

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