Identification and Quantification of Alkylketene Dimers by Pyrolysis–Gas Chromatography/ Mass Spectrometry and Pyrolysis–Gas Chromatography/ Flame Ionization Detection

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The various questions and problems related to the enhanced application of synthetic sizes demand analytical methods to characterize these sizes in paper. For this purpose, pyrolysis–gas chromatography/flame ionization detection (Py–GC/FID) and pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS) have been investigated. Examples are the analysis of samples treated with an unknown alkylketene dimer (AKD) type and the influence of $CaCO_3$ on the pyrolytic results. With Py–GC/MS, the simultaneous quantification of AKD and other additives in paper is possible if the analysis is based on pyrolytic degradation products of AKD. When the Py–GC/FID technique is applied, the area ratios of the corresponding AKD ketone peaks can be used to determine the composition of the AKD grade, and the same correlation can be used to establish a universal calibration. This calibration enables the quantification of a broad range of AKD compositions with only one calibration.

Pour caractériser les colles synthétiques dans le papier, il faut des méthodes d'analyse permettant d'en améliorer l'application. À cette fin, nous avons évalué les méthodes chromatographie à pyrolyse/détection à ionisation de flamme (Py–GC/FID) et chromatographie à pyrolyse/ spectrométrie de masse (Py–GC/MS). On peut donner comme exemple l'analyse d'échantillons traités avec un type d'alkylkétènedimère (AKD) inconnu et l'influence du $CaCO_3$ sur les résultats pyrolitiques. Avec la méthode Py–GC/MS, la quantification simultanée de l'AKD et d'autres additifs dans le papier est possible si l'analyse est basée sur les produits de la dégradation pyrolytique de l'AKD. Lorsque la technique Py–GC/FID est appliquée, les rapports de surface des crêtes de cétone d'AKD peuvent être utilisés pour déterminer la composition de la classe d'AKD, et cette même corrélation peut être utilisée pour établir une référence universelle. Cette référence permet la quantification d'une variété de compositions AKD à l'aide d'une seule référence.

INTRODUCTION

A major trend in the production of graphic papers is the change from acidic to neutral or weakly alkaline processes. The main advantage of using these pH conditions is that $CaCO_3$ can be used as a cost-efficient filler. To achieve the hydrophobicity necessary for graphic paper grades under neutral to alkaline conditions, synthetic agents like alkylketene dimers (AKD) and alkenyl succinic anhydride are used because of their specific sizing efficiency, which is much better than that of conventional rosin or modified rosin sizes. Therefore, there is also a trend to substitute these synthetic sizing agents for rosin-based sizes. According to Roberts [1], only 20% of the sized paper produced worldwide is treated with rosin-based sizes. Regarding the application of synthetic sizes, important questions and problems are still open or have to be solved. Examples are the type of bonding between fibres and AKD [2,3], and the rather low retention of AKD [2,4]. To investigate these items, analytical methods are necessary to identify and quantify the synthetic sizing agents in paper. Various methods have been described for AKD quantification. The most common method, a combination of solvent extraction and subsequent chromatographic analysis [5], is time and solvent consuming and therefore relatively expensive. To avoid these problems connected with tedious sample preparation, indirect methods were also proposed using fluorescent dyes for AKD detection [1]. Analytical pyrolysis in combination with gas chromatography (pyroly-

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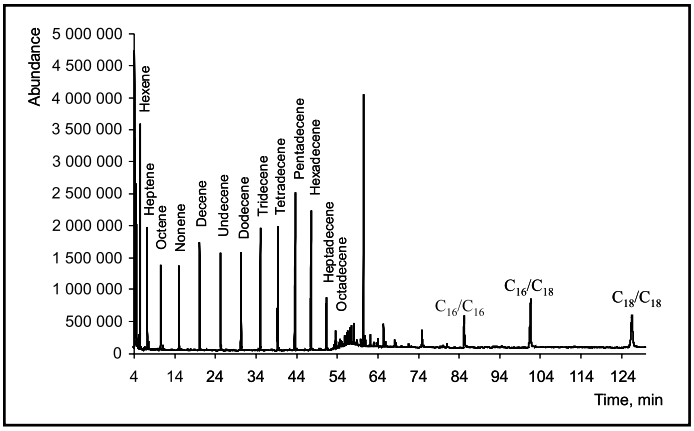

Fig. 1. Pyrogram of AKD (C_{16}:C_{18} = 50:50).

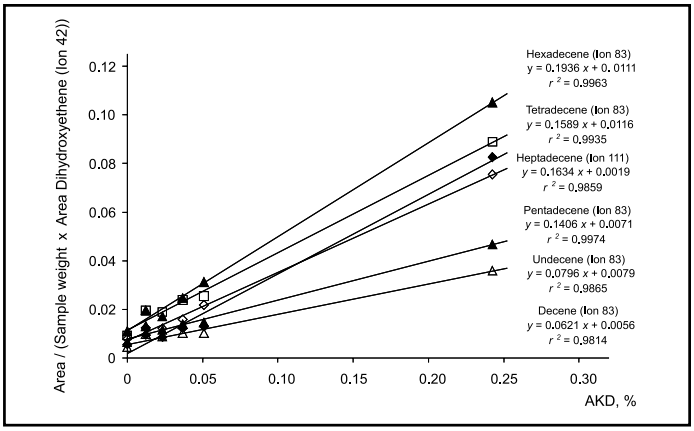

Fig. 2. Calibration curves based on key ions of various alkenes. The dependent variable is the peak area of the key ions standardized against the weight of pyrolysis samples and in relation to the peak area of ion 42, which is a characteristic ion within the mass spectra of the pyrolytic degradation product dihydroxyethene. Dihydroxyethene derives from the fibre matrix and is a typical pyrolysis product of cellulose. In this case, it serves as an internal standard.

sis–gas chromatography/flame ionization detection) (Py–GC/FID) has proven to be a valuable tool for the quantification of AKD, especially because of the much easier and faster steps before the chromatographic separation [6–9]. To apply Py–GC/FID, the AKD type used has to be known and, for each AKD grade, a specific calibration is necessary [8].

In this paper, some aspects using analytical pyrolysis for identification and quantification of AKD are investigated. The published methods are based on the corresponding ketone peaks of the AKDs and it is stated that the AKD under investigation has to be known. In this paper it is shown that, when using a Py–GC/MS system, the quantification can be done also with the pyrolytic degradation products. In addition, it is also shown how the relative peak intensities in the pyrograms can be used to calculate the AKD composition and to establish a kind of universal calibration for the quantification of a wide range of AKD grades by Py–GC/FID.

EXPERIMENTAL

An industrial spruce sulphite pulp was used as matrix material. The three AKD samples investigated were produced from palmitic (16 C atoms) and stearic acid chlorides (18 C atoms) and differ only in their C_{16}/C_{18} ratio. The AKD samples were kindly supplied by BASF AG, Ludwigshafen, Germany. The following ratios were used:

— AKD I : C_{16}/C_{18} = 35/65;
— AKD II: C_{16}/C_{18} = 50/50;
— AKD III: C_{16}/C_{18} = 0/100.

Paper samples were prepared from handsheets produced according to Zellcheming standard V/8/76 [10]. $CaCO_3$-containing paper samples were produced by adding 20% $CaCO_3$ (Hydrocarb OG, Omya, Inc., Proctor, VT, USA) based on oven-dry pulp to a pulp suspension of ~2.5% consistency. After mixing for 5 min in an Ultraturax stirrer, the suspension was diluted according to the Zellcheming standard for handsheet production (V/6/61) [11]. The $CaCO_3$ content in the sheets was measured according to TAPPI Test Method T 211 [12]. An amount of 125 µL AKD solution, with adjusted AKD concentration and toluene as the solvent, was applied to both sides of 150 mg pieces of paper with a microlitre syringe. After removal of the solvent at 90°C for 30 min in a ventilated oven, the 150 mg pieces were cut into smaller pieces and milled in a vibration ball mill (from Retsch GmbH, Haan, Germany) for 60 min to a fine powder. This powder was the starting material for the analytical pyrolysis. Pyrolysis was conducted with a filament pyrolyzer from CDS (Chemical Data Systems, Analytical, Inc., Oxford, PA, USA), Pyroprobe 100. The pyrolysis conditions were as follows: 550°C pyrolysis temperature (adjusted at the pyrolysis controller), 280°C pyrolysis interface temperature and 10 s pyrolysis time. The pyrolysis unit was mounted on a Hewlett-Packard 6890 GC with an Hewlett Packard 5972A mass selective detector (MSD). For the GC/MS system, the following conditions were used:

— Column DB 1701 from Chrompack, Palo Alto, CA, USA (60 m x 0.25 mm, 0.25 µm film);
— Constant flow rate of 1 mL/min;
— Oven program of 4 min at 45°C/3°C per min to 280°C/15 min at 280°C (or longer);
— Injector temperature 350°C;
— Split was set at 30:1 for full scan and 10:1 for selective ion monitoring (SIM) mode.

The same pyrolysis unit was used with a Chrompack CP 9000 GC equipped with a flame ionization detector (FID). The pyrolysis interface temperature was set at 290°C and the pyrolysis temperature was set at 700°C (adjusted at the pyrolysis controller). The GC/FID conditions were:

— Column DB 1 from Chrompack (30 m x 0.25 mm, 0.25 µm film);
— Oven program from 50°C with 10°C/min to 325°C/10 min at 325°C;
— 350°C injector temperature;
— 350°C detector temperature.

Fluoranthene was used as the internal standard. Just before the analytical pyrolysis, 4 µL of a fluoranthene solution, 0.2 mg fluoranthene/mL acetone, was injected into the pyrolysis interface.

RESULTS AND DISCUSSION

Quantification of AKD by Py–GC/MS

The pyrogram for pure AKD can be divided into two regions (Fig. 1). At retention times of 80 to 130 min there are three peaks, C_{16}/C_{16}, C_{16}/C_{18} and C_{18}/C_{18}, which represent the ketones formed from the corresponding AKD by rearrangement and decarboxylation during sheet preparation and storage or during the Py–GC analysis [3,8]. As the AKDs investigated here were produced from palmitic (16 C atoms) and stearic (18 C atoms) acids, the three peaks represent the ketones resulting from the possible combination of these two components in AKD: C_{16}/C_{16}, $C_{16}/_{18}$ and C_{18}/C_{18}. These three peaks are normally used for the quantification of AKD in paper products [6,9]. Hence, a part of the AKD is not broken down to smaller units during the pyrolysis of the sample and survives the high temperatures more or less unchanged.

The first part of the pyrogram in Fig. 1, from ~4 to ~60 min, is dominated by the pyrolytic degradation products from AKD, consisting mainly of the homologous series of alkenes which are formed when long-chain fatty acids are pyrolyzed. If the measurements are done under identical conditions, the formation of these degradation products is highly reproducible. When applying the SIM mode of the MSD, suitable ions from the mass spectra of the alkenes can be used to detect and quantify AKD in paper samples (Fig. 2), in a way similar to that demonstrated earlier for polyamidoamino–epichlorohydrin resins (PAAE) and polyacrylamide (PAM) [13,14]. The two main advantages of using the SIM mode of the MSD is the better signal to noise ratio and the fade out of potential superposition with pyrolytic products from the matrix. The calibration curves in Fig. 2 show relatively high correlation coefficients which are sufficient for quantification purposes. Satisfactory correlation coefficients could only be achieved by using a typical cellulose degradation product, dihydroxyethene, as

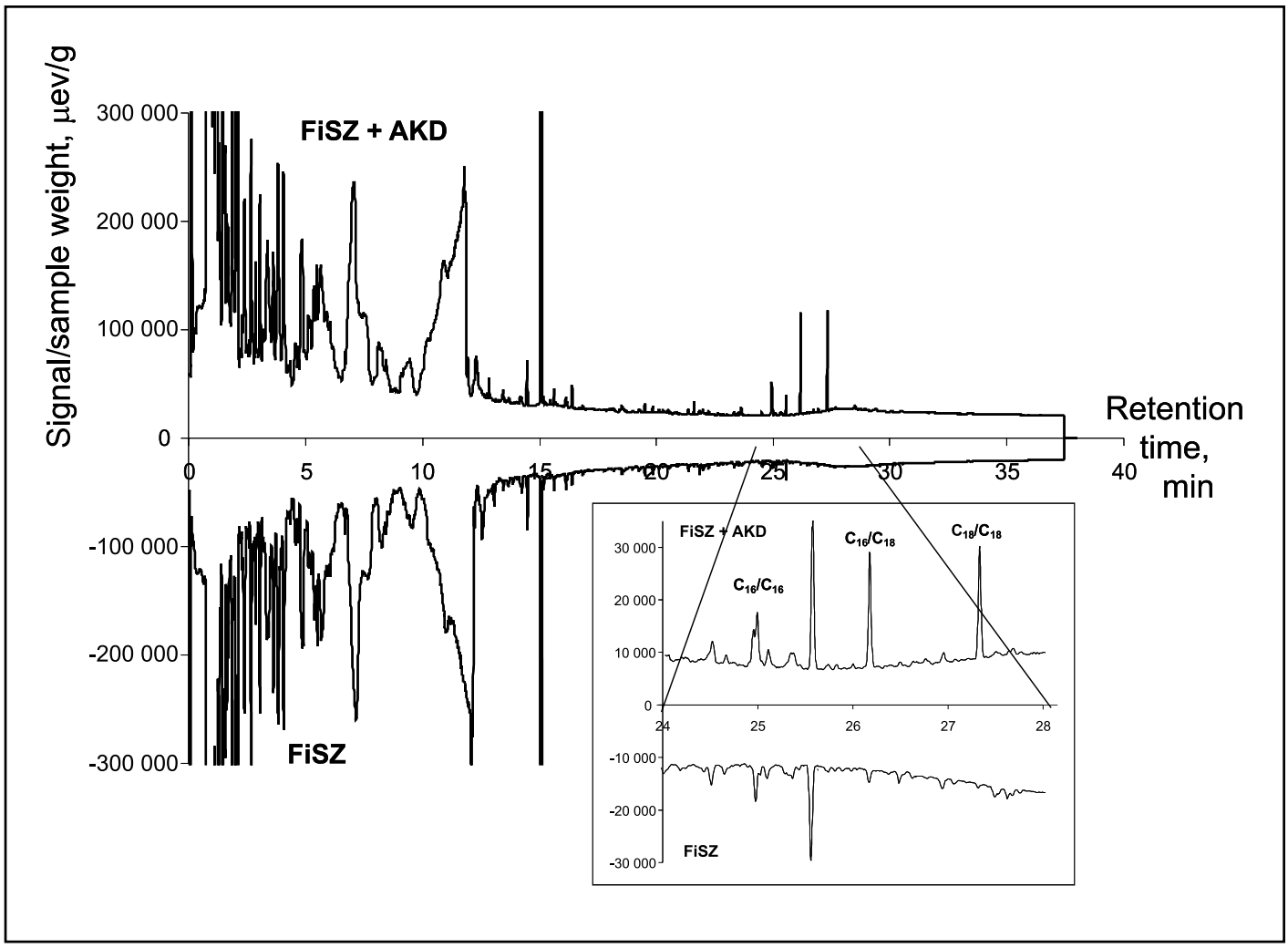

Fig. 3. Comparison of pyrograms of FiSZ (spruce sulphite pulp) and FiSZ where AKD was added.

the internal standard (see caption of Fig. 2).

Using key ions from the mass spectra of pyrolytic degradation products of AKDs and of other additives, like PAAE, PAM and AKD which elute at different retention times, enables the detection and quantification of these additives in a single Py–GC/MS measurement. The major drawback of this procedure is that there are relatively strong signals when no AKD is added. Presumably, there is a superposition with the degradation products of the fibre matrix. From spruce sulphite pulp, which was used as the fibre matrix, it is known that the removal of hydrophobic extractives during cooking is much lower than in the case of kraft pulp, since sulphite pulp is produced under acidic conditions, in contrast to the strong alkaline conditions of the kraft process. It can be assumed that the superposition is likely an impact of residual long-chain extractives within the pulp, like waxes, fats and others. Another disadvantage is the tendency for the buildup of impurities when AKD-containing samples were pyrolyzed, especially when using a semi-polar column which has a relatively low temperature resistance. In general, it can be stated that a concomitant quantification of different additives, including AKD, is possible when the base level of the typical pyrolytic degradation products of long-chain hydrocarbons at 0% AKD addition is known. That means that this base level, which is presumably produced from wood extractives, must be measured by Py–GC/MS and, for that reason, the matrix material must be available. But when analyzing unknown samples, it is difficult to differentiate between these two sources, AKD and wood extractives, which result in the same pyrolytic degradation products.

Quantification with Py–GC/FID

Py–GC/FID for AKD analysis is possible because the ketones derived from AKD are very different in molecular weight and surface characteristics from the pyrolytic products of the paper matrix and the AKD. They can be separated easily via GC (Fig. 3). Nearly all of the pyrolysis products of the fibres and the AKD elute during the first 15 min under the conditions chosen for the GC separation. The characteristic ketone peaks C_{16}/C_{16}, C_{16}/C_{18} and C_{18}/C_{18} elute between 25 and 28 min. After the big and poorly resolved peak for levoglucosan at ~11 min, the peak of fluoranthene can be seen at ~15 min. Fluoranthene was applied as the internal standard, but the reproducibility when using the internal standard was lower than without it. Therefore, fluoranthene was not taken into account for calibration in Figs. 4–6.

Figures 4–6 show calibration curves based on the three different ketones of the AKD grades investigated. In addition, papers were prepared with different AKD contents and ~13% $CaCO_3$ filler to see if there is an influence on the pyrolytic behaviour. It is known from investigations on the pyrolysis of wood and fibres that certain metals catalyze reactions during pyrolysis, resulting in different amounts of pyrolysis products [15]. Using the peaks C_{16}/C_{16}, C_{16}/C_{18} and C_{18}/C_{18}, the correlation coefficients of the calibration curves are higher than even in the case described in Fig. 2, in which the pyrolytic degradation products were used. There are only minor problems with superposition with matrix products, as indicated by the low base levels at 0% AKD addition. Only the evaluation of peak C_{16}/C_{16} was somewhat difficult because of superposition with a matrix product. No adjustment of the chromatographic conditions was undertaken to improve the separation, because the quantification could be done based on the other two peaks. As can be seen in Figs. 4–6, there is no influence of the $CaCO_3$ input. The different slopes of the calibration curve for the different AKD grades are obvious, which normally makes a separate

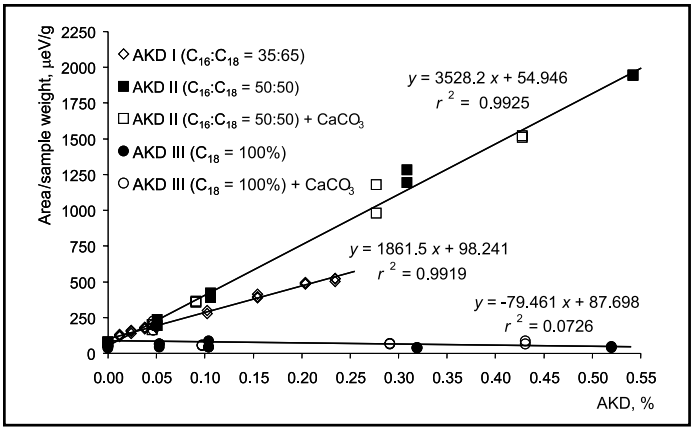

Fig. 4. Calibration curves based on peak C_{16}/C_{16} of Fig. 1 for various AKD grades. The dependent variable is the peak area of peak C_{16}/C_{16} standardized against the weight of the pyrolysis sample without $CaCO_3$.

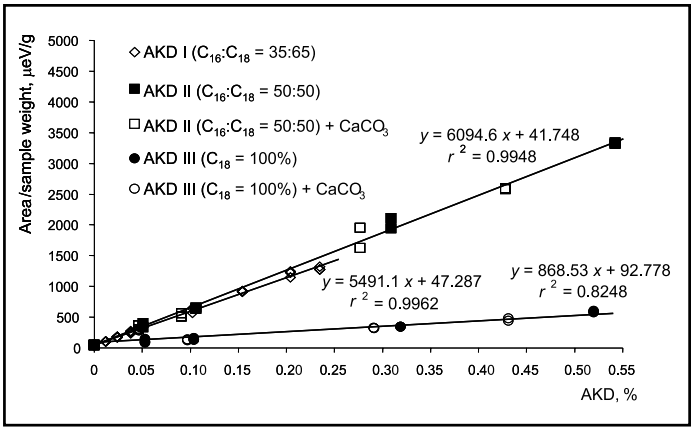

Fig. 5. Calibration curves based on the peak C_{16}/C_{18} of Fig. 1 for various AKD grades. The evaluation is comparable to Fig 4.

calibration for each AKD necessary. As the three AKD grades investigated differ only in their C_{16} and C_{18} chain contents, the differences in the area ratios of peaks C_{16}/C_{16}, C_{16}/C_{18} and C_{18}/C_{18} must represent the differences in AKD composition.

Table I shows what the area ratios must be at known AKD compositions. Assuming that there is a statistical combination of the fatty acid chlorides during AKD production, a probability of 0.5 x 0.5 = 0.25 exists in the case of equal molar fraction (50% palmitic acid and 50% stearic acid) for the formation of C_{16}/C_{16} and C_{18}/C_{18} AKD. That means that the final AKD product consists of 25% C_{16}/C_{16}–lactone, 25% C_{18}/C_{18}–lactone and 50% C_{16}/C_{18}–lactone, since there is no way to distinguish between C_{16}/C_{18} and C_{18}/C_{16}. Based on this assumption, the composition of an unknown AKD can be derived from the area ratios of the ketone peaks C_{16}/C_{16}, C_{16}/C_{18} and C_{18}/C_{18}, as demonstrated in Table II. Here, the sum of the ketone peak areas of the peaks C_{16}/C_{16}, C_{16}/C_{18} and C_{18}/C_{18} in the measured pyrogram of an AKD with a C_{16}/C_{18} composition of 50:50 was set as 100%. Calculating the square root of the measured area shares of the peaks C_{16}/C_{16} and C_{16}/C_{18} gives the composition of the AKD.

In a similar way, it is possible to calculate the slope of the calibration curves for the single ketones. This is demonstrated in Table III for the C_{18}/C_{18} peak. Only one calibration of an AKD sample with known fatty acid composition is necessary to calculate the slope for the calibration curves of all other AKD compositions containing C_{18}. For example, the slope of the calibration curve based on the C_{18}/C_{18} peak of an AKD consisting of pure C_{18}/C_{18}–lactone was calculated as 12 989. An AKD with a C_{18}/C_{18} content of 80% must give an area ratio of 64% (0.8 x 0.8 = 0.64). Then, the slope of the calibration curve also must be 64% of 12 989 = 8313. The data from Table III are plotted in Fig. 7. The starting point was the calibration curve of peak C_{18}/C_{18} measured for the AKD consisting of 100% C_{18}/C_{18}–lactone, where the slope was calculated as 12 989. For verification, the slopes of the calibration curves based on the measurements of the other two AKD samples with 50 and 65% C_{18} content were also plotted in Fig. 7 and fit very well with the calculated values.

An easier way to quantify AKD with known components but unknown composition is to take the sum of the peak areas of the peaks C_{16}/C_{16}, C_{16}/C_{18} and C_{18}/C_{18} for calibration (Fig. 8). This has been proposed in other investigations [8,9]. Figure 8 shows that this can be done even if one has to deal with different AKD compositions. Stearic acid and palmitic acid are the most widespread raw materials for AKD production. If fatty acids other than palmitic

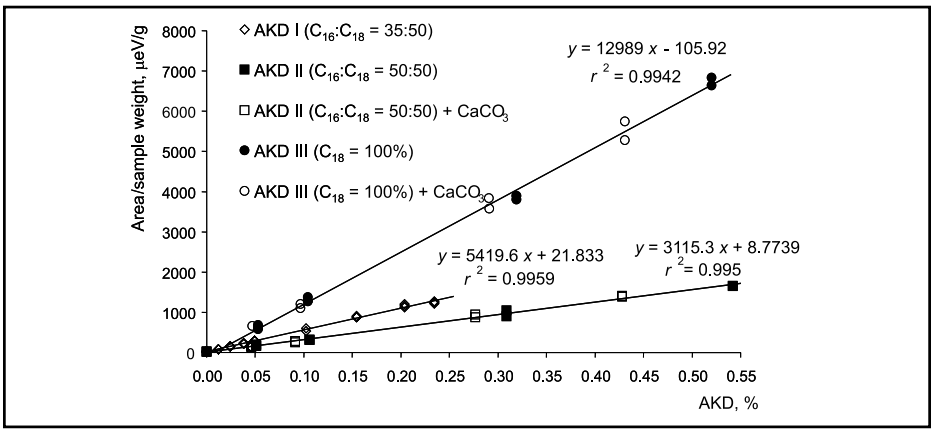

Fig. 6. Calibration curves based on the peak C_{18}/C_{18} of Fig. 1 for various AKD grades. The evaluation is comparable to Fig. 4.

TABLE I
DEPENDENCE OF AKD COMPOSITION AND AREA RATIOS OF THE KETONE PEAKS IN PYROGRAMS

AKD II				
Share at production	C_{16} 50%		C_{18} 50%	
Probability of combination	C_{16}/C_{16} 25%	C_{16}/C_{18} 25%	C_{18}/C_{16} 25%	$C_{18}/C18$ 25%
Composition of final product	C_{16}/C_{16} 25%	C_{16}/C_{18} + C_{18}/C_{16} 50%		C_{18}/C_{18} 25%
AKD I				
Share at production	C_{16} 35%		C_{18} 65%	
Probability of combination	C_{16}/C_{16} 12%	C_{16}/C_{18} 23%	C_{18}/C_{16} 23%	C_{18}/C_{18} 43%
Composition of final product	C_{16}/C_{16} 12%	C_{16}/C_{18} + C_{18}/C_{16} 46%		C_{18}/C_{18} 43%

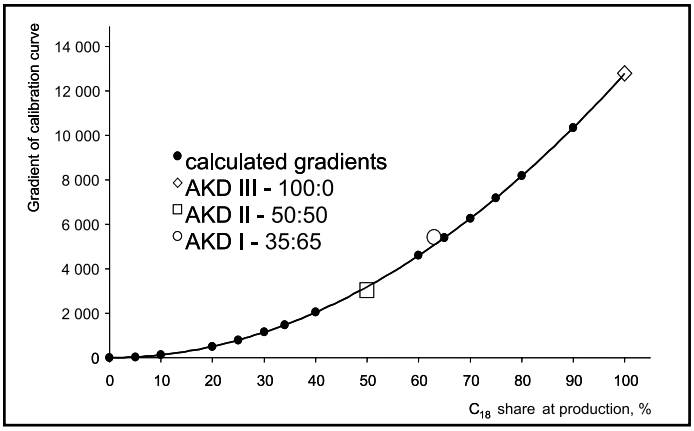

Fig. 7. Gradient of the calibration curve for peak C_{18}:C_{18} in relation to AKD composition.

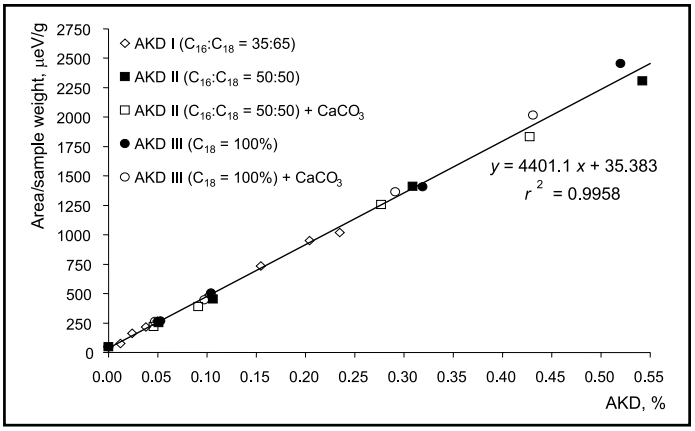

Fig. 8. Calibration based on the sum of the peak areas of the peaks C_{16}/C_{16}, C_{16}/C_{18} and C_{18}/C_{18}.

TABLE II
EXAMPLE OF THE CALCULATION OF AKD COMPOSITION FROM AREA RATIOS OF THE PEAKS C_{16}/C_{16}, C_{16}/C_{18}, C_{18}/C_{18} FROM THE PYROGRAM OF AN AKD WITH A C_{16}:C_{18} COMPOSITION OF 50:50

	C_{16}/C_{16}	C_{16}/C_{18}	C_{18}/C_{18}	Σ
Peak area	57 185	85 665	42 554	185 404
Area share	31%	46%	23%	100%
	C_{16}		C_{18}	Σ
AKD composition	$x = \sqrt{\text{area share}}$ $= \sqrt{0.31} = 0.56 = 56\%$		$x = \sqrt{\text{area share}}$ $= \sqrt{0.23} = 0.48 = 48\%$	104%

TABLE III
THEORETICAL CALCULATION OF THE GRADIENT OF THE CALIBRATION CURVE FOR PEAK C_{18}/C_{18} FROM THE AKD COMPOSITION

C_{18} share at production	C_{18}/C_{18} share in AKD	Slope of calibration curve
100	100	12 989
90	81	10 521
80	64	8 313
70	49	6 365
65	42.25	5 488
60	36	4 676
50	25	3 247
40	16	2 078
35	12.25	1 591
30	9	1 169
20	4	520
10	1	130
0	0	0

and stearic acid are used, similar peaks can be detected, but at different retention times, and the same calculations can be done.

CONCLUSIONS

Analytical pyrolysis is well suited for the identification and quantification of AKD. During pyrolysis, AKD is partly degraded into smaller fragments and another part can be detected in the form of the corresponding ketones. Applying various techniques, both groups of products can be used for quantification. With Py–GC/MS, the degradation products can be used for quantification by applying the SIM mode to enhance the signal-to-noise ratio and to fade out matrix products. When using Py–GC/MS in the way described above, the results are more reliable when there is a possibility of measuring also the matrix without any AKD. Applying Py–GC/FID, the relative intensities of the characteristic ketone peaks give information on the composition of the parent AKD. Knowing the composition makes the establishment of a universal calibration possible, which enables the quantification of a whole range of different AKDs with only one calibration.

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