The influence of amino chain length and calcium lignosulfonate modification on lignosulfonamides flammability and thermal stability

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Abstract: The influence of methods for obtaining lignosulfonyl chloride (through chemical modifications of calcium lignosulfonate) and the amine chain length on the thermal properties and flammability of lignosulfonamides were examined. HCl/HSO_3Cl, HCl/PCl_5, PCl_5, and $SOCl_2$ were used to calcium lignosulfonate modification. The conditions for the synthesis of lignosulfonamides were optimized. Promising results were aquired for *N*-butyl-*N*-dodecyl-lignosulfonamides obtained by reaction with thionyl chloride and PCl_5. Tests confirmed negligible flammability and better thermal stability. The obtained lignosulfonamides can be used as flame-retardants in biocomposites.

Keywords: lignosulfonamides, calcium lignosulfonate, lignosulfonyl chloride, flame-retardants, biomaterials.

Wpływ długości łańcucha aminowego i modyfikacji lignosulfonianu wapnia na palność i stabilność termiczną lignosulfonamidów

Streszczenie: Zbadano wpływ metod otrzymywania chlorku lignosulfonylu (poprzez modyfikację chemiczną lignosulfonianu wapnia) oraz długości łańcucha aminowego na właściwości termiczne i palność lignosulfonamidów. Do modyfikacji lignosulfonianu wapnia zastosowano HCl/HSO_3Cl, HCl/PCl_5, PCl_5 i $SOCl_2$. Zoptymalizowano warunki syntezy lignosulfonamidów. Obiecujące wyniki uzyskano dla *N*-butylo-*N*-dodecylo-lignosulfonamidów otrzymanych w reakcji z chlorkiem tionylu i PCl_5. Badania potwierdziły znikomą palność i lepszą stabilność termiczną. Otrzymane lignosulfonamidy można stosować jako środki zmniejszające palność biokompozytów.

Słowa kluczowe: lignosulfonamidy, lignosulfonian wapnia, chlorek lignosulfonylu, środki zmniejszające palność, biomateriały.

Lignosulfonamides, amides of organosulfonic acids, are a group of organic compounds of natural origin. Compared to other flame retardants (especially synthetic ones) containing phosphorus-nitrogen groups in their chemical structure, sulfonamides probably have autocatalytic properties, e.g., condensation, which are activated at elevated temperatures (several dozen degrees above biopolymer flow temperature).

Lignosulfonate derivatives can be obtained by chemical modification of calcium lignosulfonate, which is a byproduct of the pulp and paper industry [1–3]. Some of the common chemical modifications include sulfonation, acetylation, esterification, cross-linking, and polymerization [4–7]. Calcium lignosulfonate is sulfonated to improve its water solubility and dispersibility. This modification can be achieved by treating calcium lignosulfonate with sulfuric acid or oleum. Acetylation (e.g., with acetic anhydride) reduces water solubility and improves stability in certain environments. Esterification with anhydrides or carboxylic acid chlorides aims to introduce new functional groups into the structure, which improves properties in some applications. Cross-linking using e.g., formaldehyde or glutaraldehyde increases stability and resistance to degradation. Calcium lignosulfonate can also be polymerized to improve its properties in certain applications using polymerization initiators such as peroxides or azo compounds.

These chemical modifications can be used to tailor the properties of calcium lignosulfonate to specific applications such as construction, agriculture, or the food industry. However, the potential impact of these modifications on the environment and human health should be considered. They must be used responsibly [8–11].

Flame retardants are added to improve the fire resistance of the materials. Commonly used flame retardants for poly-

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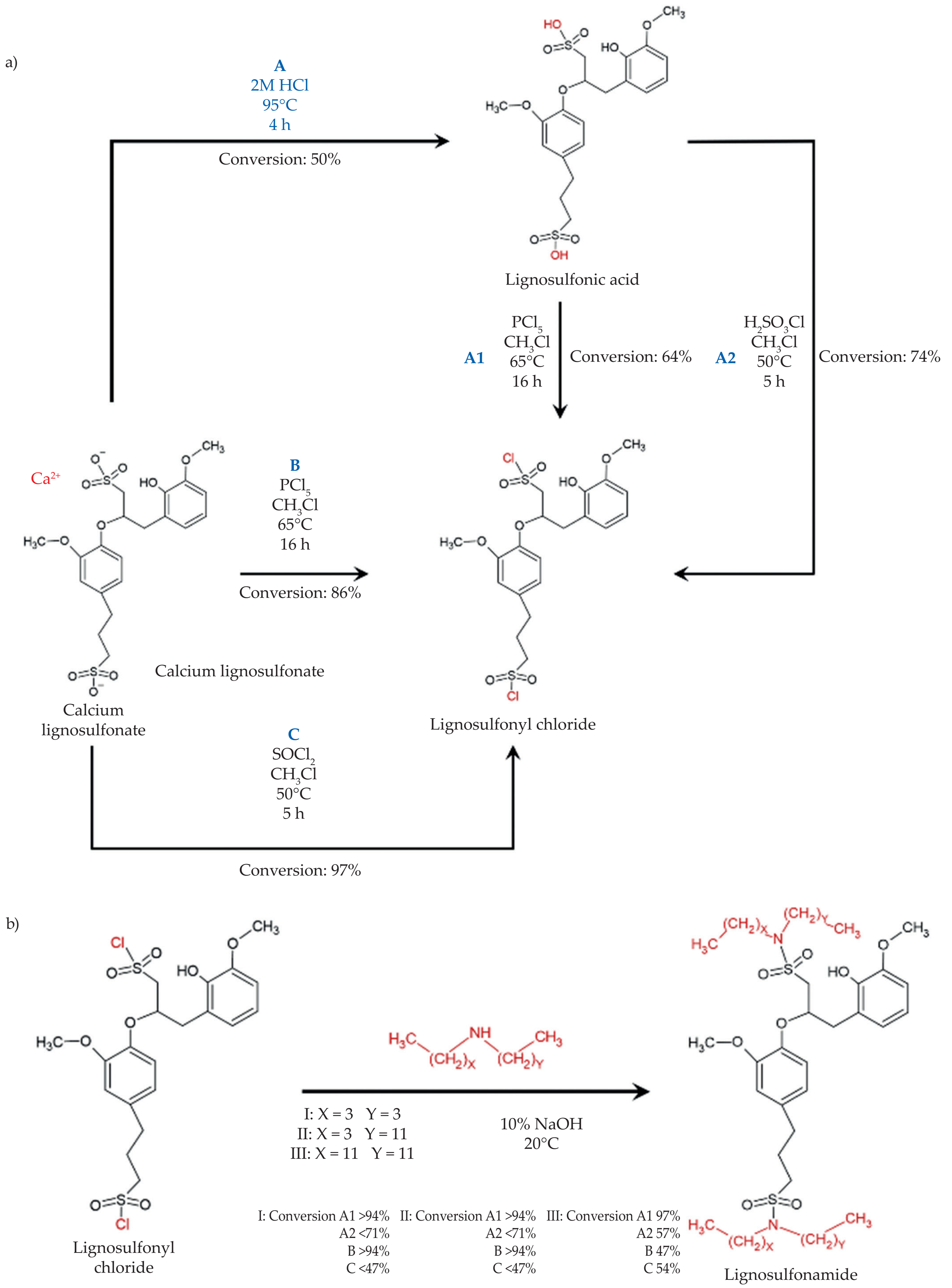

Fig. 1. Two-stage process for obtaining lignosulfonamides: a) modification of calcium lignosulfonate (lignosulfonyl chloride syntheses), b) lignosulfonamides synthesis

mers include halogen (chlorine, bromine, fluorine), mineral (aluminum trihydrate, magnesium hydroxide, zinc borate), nitrogen- (e.g., melamine and guanidine) and phosphorus-based compounds [12–15]. Halogen flame retardants work by creating free radicals during the combustion process, which end the chain reaction and slow down the combustion process. Mineral flame retardants release water or non-flammable gases when heated, cooling the polymer, and inhibiting the combustion process. Nitrogen- and phosphorus-based flame retardants work similarly by releasing gases (containing nitrogen and phosphorus, respectively), which dilute the flammable gases produced by the polymer. Phosphorus-based flame retardants are the most used flame retardants in engineered biopolymers.

Some flame retardants may cause environmental or health risks, so it is important to use them responsibly. Moreover, the type and concentration of flame retardants should be selected to ensure an optimal balance between fire resistance and other performance properties of the biopolymer [16–17].

An effective method for the synthesis of selected lignosulfonamides was developed. The obtained biomaterials were tested using thermogravimetric analysis (TGA) and calorimetry test (MCC).

EXPERIMENTAL PART

Materials

Calcium lignosulfonate (Lignobind type 1, industrial grade) in the form of brown powder was supplied by Penquisa (Beriain, Spain). Chloroform (analytical grade), thionyl chloride (reagent grade), phosphorus pentachloride (reagent grade), sodium hydroxide (analytical grade) was purchased from Sigma Aldrich (Darmstadt, Germany). Hydrochloric acid of analytical purity (35–38 wt%) was purchased from Chempur (Piekary Śląskie, Poland). Dibutylamine, *N*-butyl-*N*-dodecylamine, and didodecylamine were purchased from Sigma-Aldrich (Darmstadt, Germany). All the chemicals were used as received.

Preparation of lignosulfonamides

The process of obtaining lignosulfonamides was carried out in two stages. The first stage consisted of the reaction of calcium lignosulfonate (CaL) with selected organochlorine reagents (HCl/HSO_3Cl, HCl/PCl_5, PCl_5, and $SOCl_2$) to obtain lignosulfonyl chloride (LCl), which in the second stage reacted with secondary amines having in their structure: i) two short aliphatic chains with 4 carbon atoms (dibutylamine, DBA), ii) one short aliphatic chain with 4 carbon atoms and one long aliphatic chain with 12 carbon atoms (*N*-butyl-*N*-dodecylamine, BDA) and iii) two long aliphatic chains with 12 carbon atoms (didodecylamine, DDA). The reaction conditions and yield are shown in Figure 1.

CaL modification with hydrochloric acid (Reaction A – yield 50%)

200 g of CaL, dried at 90°C for 24 h under vacuum, was put into a round-bottom flask, and then 500 mL of 2 M HCl was introduced into the vessel. The mixture was heated to 95°C and reacted for 4 h. After cooling to room temperature, the mixture was concentrated using a rotary evaporator at 90°C, at rotation speed 50 rpm, under pressure of 200 mbar until the desired degree of evaporation. The resultant sludge was further dehydrated in a desiccator over magnesium sulfate at room temperature. The product was dried under ambient conditions to constant weight and ground with porcelain mortar. Prepared lignosulfonic acid (LA) was byproduct to the next reaction with phosphorus pentachloride (PCl_5) or chlorosulfonic acid (HSO_3Cl) resulting in the formation of lignosulfonyl chloride.

Table 1. Lignosulfonamides obtained within chemical modification of CaL

First step				Second step			Sample
HCl	HSO_3Cl	$SOCl_2$	PCl_5	DBA	BDA	DDA	
+	+	–	–	+	–	–	LCl-ACS-DBA
+	+	–	–	–	+	–	LCl-ACS-BDA
+	+	–	–	–	–	+	LCl-ACS-DDA
+	–	–	+	+	–	–	LCl-AP-DBA
+	–	–	+	–	+	–	LCl-AP-BDA
+	–	–	+	–	–	+	LCl-AP-DDA
–	–	–	+	+	–	–	LCl-P-DBA
–	–	–	+	–	+	–	LCl-P-BDA
–	–	–	+	–	–	+	LCl-P-DDA
–	–	+	–	+	–	–	LCl-Th-DBA
–	–	+	–	–	+	–	LCl-Th-BDA
–	–	+	–	–	–	+	LCl-Th-DDA

LA modification with phosphorus pentachloride (Reaction A1 – yield 64%)

35 g of LA and 30 g of PCl_5 were placed in a round-bottom flask and mixed. Then, the vessel was equipped with a condenser, and 400 mL of $CHCl_3$ was added to the mixture. After reaching 65°C, the reaction was continued for 16 h. After cooling to room temperature, the mixture was placed in a rotary evaporator and concentrated until the desired degree of evaporation (50°C, 50 rpm, 700 mbar). Then, the obtained lignosulfonyl chloride (LCl-AP) was dried at 60°C to constant weight.

LA modification with chlorosulfonic acid (Reaction A2 – yield 74%)

50 g of LA with 650 mL of $CHCl_3$ was placed in a round-bottom flask equipped with a condenser, submerged in cold water. Then, 20 mL of HSO_3Cl was added in small quantities while keeping the temperature below 50°C. After the addition of HSO_3Cl temperature was kept at 50°C, and the reaction was carried out for 5 h. The contents of the flask were cooled to room temperature and then concentrated using a rotary evaporator at 50°C, at 50 rpm, under pressure of 500 mbar. The resultant sludge containing lignosulfonyl chloride (LCl-ACS) was dried at 60°C to constant mass.

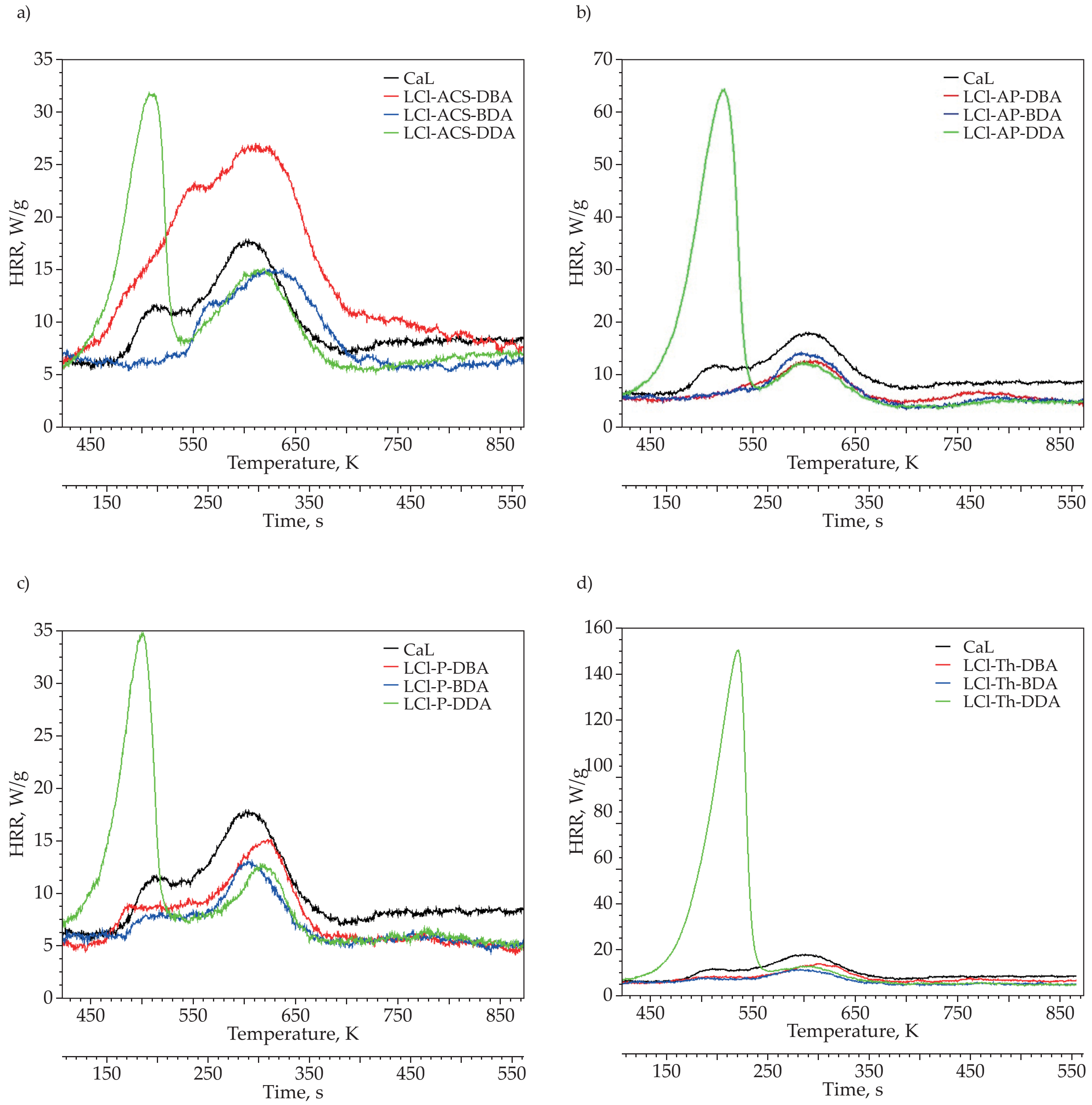

Fig. 2. HRR vs. temperature curves for lignosulfonamide samples obtained by different modification method: a) HCl and HSO_3Cl modification (ACS), b) HCl and PCl_5 modification (AP), c) PCl_5 modification (P), d) $SOCl_2$ modification (Th)

T a b l e 2. Flammability factors for lignosulfonamides; PHR – maximum peak heat release, TTI – time to ignition, TOF – flameout time

Sample	PHR W/g	TTI		TOF		Combustion time s
		s	K	s	K	
CaL	18	162	473	504	821	342
LCl-ACS-DBA	27 ↑	114 ↓	425	543 ↑↑	849	429 ↑↑
LCl-ACS-BDA	15 ↓	200 ↑↑	522	422 ↓↓	748	222 ↓↓
LCl-ACS-DDA	32 ↑	105 ↓↓	425	390 ↓↓	705	285 ↓
LCl-AP-DBA	12 ↓	144 ↓	458	530 ↑	849	386 ↑
LCl-AP-BDA	14 ↓	155 ↓	458	539 ↑	849	384 ↑
LCl-AP-DDA	63 ↑↑	93 ↓↓	423	513 ↑	849	420 ↑↑
LCl-P-DBA	15 ↓	157 ↓	464	552 ↑↑	863	395 ↑
LCl-P-BDA	13 ↓	171 ↑	483	545 ↑↑	863	374 ↑
LCl-P-DDA	35 ↑	115 ↓	423	558 ↑↑	863	443 ↑↑
LCl-Th-DBA	14 ↓	144 ↓	461	522 ↑	845	378 ↑
LCl-Th-BDA	11 ↓	160 ↓↑	474	530 ↑	849	370 ↑
LCl-Th-DDA	150 ↑↑↑	105 ↓↓	423	511 ↑	821	406 ↑↑

CaL modification with phosphorus pentachloride (Reaction B – yield 86%)

50 g CaL was dried at 90°C for 24 h under vacuum and then placed into a round-bottom flask with 10 g of (PCl_5 dissolved in 300 mL of chloroform and mixed. After the flask was equipped with a condenser, another 300 mL of CH_3Cl was added. Subsequently, the reagents were heated to 65°C and reacted for 16 h. The resultant suspension was cooled and concentrated in a rotary evaporator at 50°C, 50 rpm, and 700 mbar. The remaining thick suspension was dried in an oven at 60°C to obtain dry lignosulfonyl chloride (LCl-P).

CaL modification with thionyl chloride (Reaction C – yield 97%)

50 g of CaL dried at 90°C for 24 h under vacuum was placed in a round bottom flask equipped with a condenser, followed by the addition of 950 mL of $CHCl_3$. Then, 20 g of $SOCl_2$ was added in small portions to the mixture. The contents of the flask were then heated to 50°C and the reaction was carried out for 5 h. After cooling to room temperature, the mixture was concentrated using a rotary evaporator at 50°C with a 50-rpm rotating speed and under 500 mbar pressure. The obtained suspension containing lignosulfonyl chloride (LCl-Th) was dried at 60°C to constant mass.

Lignosulfonamides synthesis

All the obtained lignosulfonyl chlorides (LCl) were substrates in reaction with DBA, BDA, and DDA, respectively. In the flasks, NaOH solution, secondary diamines, and lignosulfonyl chlorides were reacted. After cooling the reaction mixtures to room temperature, a solid product was formed. The residue was filtered and washed thoroughly with distilled water and dried in ambient conditions, followed by another filtration with hot water. The solid product was dried for a few days in ambient conditions, then washed thoroughly with hot distilled water. All samples were dried in a vacuum oven at 90°C for 24 h before measurements. Obtained lignosulfonamide samples are presented in Table 1.

Methods

Micro combustion calorimetry (MCC) was performed using a Fire Testing Technology instrument (FTT, East Grinstead, UK). The tests were carried out in the temperature range of 150-750°C at a heating rate of 1°C/s in accordance with the ASTM D7309 standard. Thermogravimetric analysis (TGA) was performed using Netzsch TG 209F1 Libra analyzer (Netzsch GmbH, Selb, Germany) in the temperature range of 30–600°C, at a heating rate of 10 °C/min under both oxidative (synthetic air) atmosphere. Samples were placed in corundum crucibles.

RESULTS AND DISCUSSION

Micro combustion calorimetry analysis

The purpose of MCC is to separately characterize the anaerobic material pyrolysis and oxidation of the volatiles at the same time. The results of measuring the heat release rate as a function of time and temperature are presented in Figure 2. The analysis of heat release rate (HRR) curves shows that the obtained lignosulfonamides and reference sample are usually characterized by two main combustion stages: the first in the range of 100–250 s and the second in the range of 250–370 s. Results show that regardless of the synthesis path, for

Table 3. Calculated flammability coefficients of lignosulfonamides

Sample	Q_{max} W/g	$T_{5\%}$		$T_{95\%}$		FGC J/gK	η_c J/gK	h_c kJ/g	h_{cgas} kJ/g	Y_p %
		s	K	s	K					
CaL	18	197	507	342	655	11.85	19.99	1.03	2.36	57
LCl-ACS-DBA	27 ↑	183	483	438	743	32.95 ↑↑	30.60 ↑↑	3.56 ↑↑	6.47 ↑↑	45 ↓
LCl-ACS-BDA	15 ↓	242	565	353	678	10.20 ↓	16.44 ↓	0.81 ↓	1.07 ↓↓	24 ↓↓↓
LCl-ACS-DDA	32 ↑	149	461	328	642	23.52 ↑	35.70 ↑↑	2.02 ↑↑	3.88 ↑↑	48 ↓
LCl-AP-DBA	12 ↓	224	539	494	813	6.04 ↓↓	13.79 ↓	0.77 ↓	1.12 ↓↓	31 ↓↓
LCl-AP-BDA	14 ↓	175	477	463	772	6.85 ↓↓	15.74 ↓	0.76 ↓	1.65 ↓	54 ↓↑
LCl-AP-DDA	63 ↑↑	140	469	281	612	42.42 ↑↑	69.54 ↑↑↑	3.30 ↑↑	6.24 ↑↑	47 ↓
LCl-P-DBA	15 ↓	193	498	379	688	10.38 ↓	16.95 ↓	1.01 ↓↑	1.44 ↓	30 ↓↓
LCl-P-BDA	13 ↓	192	504	437	754	5.91 ↓↓	14.53 ↓	0.67 ↓	1.04 ↓↓	36 ↓↓
LCl-P-DDA	35 ↑	154	455	336	637	18.72 ↑	39.30 ↑↑	1.58 ↑	2.94 ↑	46 ↓
LCl-Th-DBA	14 ↓	163	480	369	689	8.87 ↓	15.22 ↓	0.86 ↓	1.31 ↓↓	34 ↓↓
LCl-Th-BDA	11 ↓	180	494	326	642	6.14 ↓↓	12.47 ↓	0.52 ↓	0.71 ↓	27 ↓↓↓
LCl-Th-DDA	150 ↑↑↑	177	482	293	600	93.92 ↑↑↑	170.37 ↑↑↑	6.75 ↑↑↑	12.69 ↑↑↑	47 ↓

where: Q_{max} – maximum value of $Q(t)$; FGC - fire growth capacity; h_c – specific heat release; h_{cgas} – specific heat of gases combustion; η_c – heat release capacity; $T_{5\%}$ – temperature at which 5% of h_c was released, measured at a heating rate β = 1 K/s; $T_{95\%}$ – temperature at which 95% of h_c was released, measured at a heating rate β = 1 K/s; Y_p – pyrolysis residue.

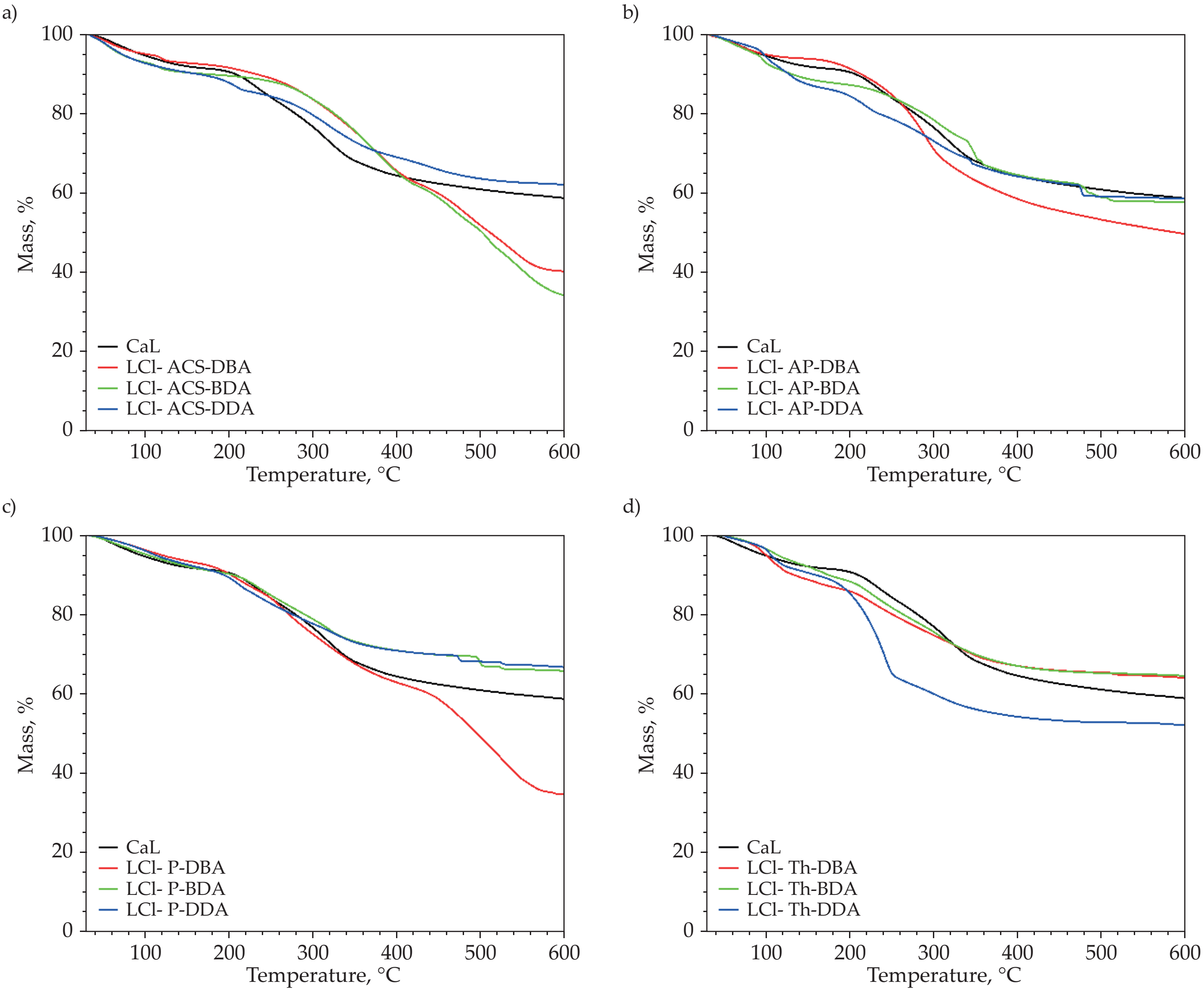

Fig. 3. TGA curves for lignosulfonamides: a) HCl and HSO_3Cl modification (ACS), b) HCl and PCl_5 modification (AP), c) PCl_5 modification (P), d) $SOCl_2$ modification (Th)

T a b l e 4. Thermogravimetric data for lignosulfonamides

Sample	$T_{5\%}$ °C	$T_{10\%}$ °C	$T_{20\%}$ °C	$T_{50\%}$ °C	T_{MAX} °C	Residue at 600°C %
CaL	94	206	278	–	315	58.6
LCl-ACS-DBA	98 ↑↓	230 ↑↑	323 ↑↑	510	375 ↑↑	40.1 ↓↓
LCl-ACS-BDA	70 ↓↓	165 ↓	325 ↑↑	501	370 ↑↑	34.0 ↓↓
LCl-ACS-DDA	71 ↓↓	159 ↓	296 ↑	–	314 ↓↑	61.9 ↑
LCl-AP-DBA	97 ↑↓	213 ↑	272 ↓↑	588	293 ↓	49.6 ↓
LCl-AP-BDA	88 ↓	130 ↓↓	288 ↑	–	350 ↑↑	57.5 ↓
LCl-AP-DDA	97 ↑↓	127 ↓↓	234 ↓↓	–	477 ↑↑	58.4 ↓↑
LCl-P-DBA	118 ↑↑	201 ↓↑	271 ↓↑	495	525 ↑↑	34.5 ↓↓
LCl-P-BDA	102 ↑	203 ↓↑	289 ↑	–	498 ↑↑	65.7 ↑
LCl-P-DDA	111 ↑↑	192 ↓	275 ↓↑	–	473 ↑↑	66.6 ↑
LCl-Th-DBA	98 ↓↑	129 ↓↓	248 ↓↓	–	104 ↓↓	63.7 ↑
LCl-Th-BDA	111 ↑↑	170 ↓	261 ↓	–	223 ↓↓	64.3 ↑
LCl-Th-DDA	104 ↑	154 ↓	217 ↓↓	–	242 ↓↓	51.2 ↓

DBAs and BDAs, the dominant combustion stage was the latter (570–670 K). However, DDAs burned very quickly, almost immediately after ignition in the first stage (400–550 K). The behavior presented in Figure 2 for the DDA samples is called nonlinear reduction. A two-peak behavior, one maximum in HRR at the beginning of burning and one at the end of burning, is observed. For samples synthesized with PCl_5, a very weak char afterburning stage can be observed in the range of 380–560 s (700–900 K).

Table 2 presents the flammability factors of pure unmodified CaL and lignosulfonamides obtained by four different modifications. It is worth noting that all tested materials are organic compounds of natural origin. Typical organic compounds are characterized by high flammability, and the biopolymers for which the obtained compounds are to be potentially used have maximum peak heat release (PHR) indicators above 600 W/g [18].

The obtained materials are characterized by a PHR coefficient in a wide range from 150 to 11 W/g. It can therefore be concluded that these materials are potentially non-flammable. The unmodified reference sample has a low PHR value, and modifications carried out especially with dibutylamine and *N*-butyl-*N*-dodecylamine resulted in a further reduction of this value.

Regardless of the CaL modification method, the use of DDA resulted in a drastic increase in the flammability of the obtained materials by 78–723%. The longest combustion time was observed for samples synthesized according to reactions A1 and B, and the shortest for samples synthesized according to reactions A2 or C. However, only in two cases it was possible to shorten the material combustion time compared to the reference sample (LCl-ACS -BDA and LCl-ACS -DDA). It was noticed that the lignosulfonamides obtained in reaction A ignited the fastest. However, only in the case of BDA a longer ignition time (TTI) was obtained than for CaL.

This preliminary analysis of flammability results proved that the most favorable changes occur after CaL modification according to paths B and C, where no HCl acid was used, as well as for samples obtained using dibutylamine and *N*-butyl-*N*-dodecylamine. The use of hydrochloric acid leads to the formation of hydroxyl groups, which may lead to the hydrolysis of the lignin derivative. Furthermore, lignosulfonamides containing two long aliphatic chains containing 12 carbon atoms were found to be more susceptible to decomposition at high temperatures than those containing two butyl chains, or one C4 and one C12 chain. To thoroughly analyze the combustion process of retained lignosulfonamides, additional factors were determined from the graphs presented in Figure 2 and are summarized in Table 3.

The above list shows the impact of the amine used for modification and the selected modification path on the overall sample combustion process. In the case of DBA, the values of the FGC, h_c, $h_{c\,gas}$, η_c and combustion time indicators can be arranged as follows according to the modification path: A2 > B > C > A1. Similarly, for BDAs, consistency in the ranking of indicator values was observed, which is as follows: A2 > A1 > B > C. This means that DBAs obtained according to reaction A2 release the most heat during the combustion of a solid substance and most heat when burning gases. The more heat is emitted, the longer the combustion process. However, DBAs obtained using the A1 method, on the other hand, release a small amount of heat and burn for a relatively short time. In turn, BDA obtained in two-step reactions A1 and A2 release large amounts of heat during the combustion of both solids and gases, while those obtained using one-step methods (B and C) release small amounts of heat, burn slowly, and produce intermediate amounts of solids residues. In turn, in the case of DDAs, the values of the FGC, h_c, $h_{c\,gas}$, η_c indicators can be arranged according to the following trend: C > A1 > A2 > B. In this case, a different relationship was

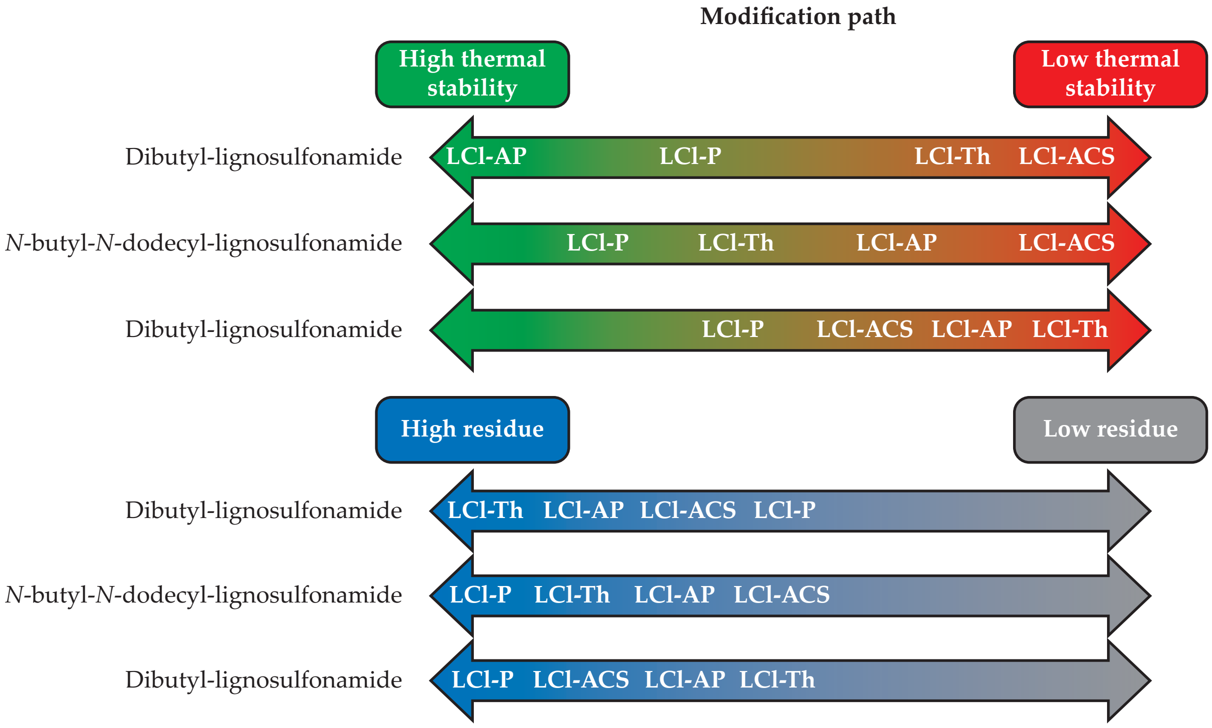

Fig. 4. The relationship between the thermal stability and the residue of lignosulfonamides in relation to various methods of calcium lignosulfonate modification

observed between the values of the above indicators and the combustion time i.e., the higher the values of the generated combustion heat, the shorter the combustion time. Therefore, the DDAs samples obtained according to reactions C and A1 burned rapidly, emitting large amounts of heat, and generating large amounts of solid residue. It should be emphasized that all the modifications carried out resulted in a reduction in the value of combustion residues in relation to CaL. Furthermore, a detailed analysis of the MCC measurement excludes the use of all DDA samples and all samples obtained in reaction A2 as flame retardants. These samples did not obtain better indicator values than the reference ones.

Thermogravimetry analysis

Figure 3 shows the results of thermogravimetric analysis of the synthesized lignin derivatives. The thermal degradation process of the CaL reference sample occurs in two stages. The first mass loss was observed around the temperature of 10% mass loss ($T_{10\%}$), and the next one at a temperature of about 360–400°C. The total weight loss did not exceed 50%. Among the LCl-ACS (A1) samples, the one containing DDA was characterized by the lowest thermal stability and the lowest mass loss. On the other hand, the best thermal stability and the highest mass loss showed the samples with DBA (Table 4).

The modification method using phosphorus pentachloride (A1) did not allow to obtain lignosulfonamides with such good thermal properties as the method using chlorosulfonic acid (A2). In comparison, LCl-AP samples were less stable up to 50% weight loss. Of the lignosulfonamides obtained, only LiCl-AP-DDA had the worst thermal stability in the entire measuring range, but also lower than LCl-ACS-DDA. Direct modification of CaL with PCl_5 allowed to obtain BDA and DDA lignosulfonamides with higher thermal stability in the whole temperature range than for the LCl-ACS and LCl-AP samples. The C modification method with thionyl chloride allowed to obtain lignosulfonamides with the lowest thermal stability. The residue indices of the LCl-Th samples were also ones the biggest in comparison to other samples. However, this does not change the fact that the one-stage C modification process leads to similar residue values at 600°C as in the case of the B modification method (Table 4).

Based on the results obtained, the dependence of the thermal stability and residues of the synthesized compounds on the amine used and the method of modification was determined. As can be seen from the data presented in Figure 4, this relationship is as follows: reaction B > reaction C > reaction A1 > reaction A2. Therefore, the relationship was confirmed only for the lignosulfonamides BDA and DDA that the larger the residue, the highest thermal stability.

MCC vs TGA

Two most key features of the material that control its fire properties are: the amount of the released gas and condensed phases and the effective heat of combustion. Reducing the amount of gaseous or condensed phases

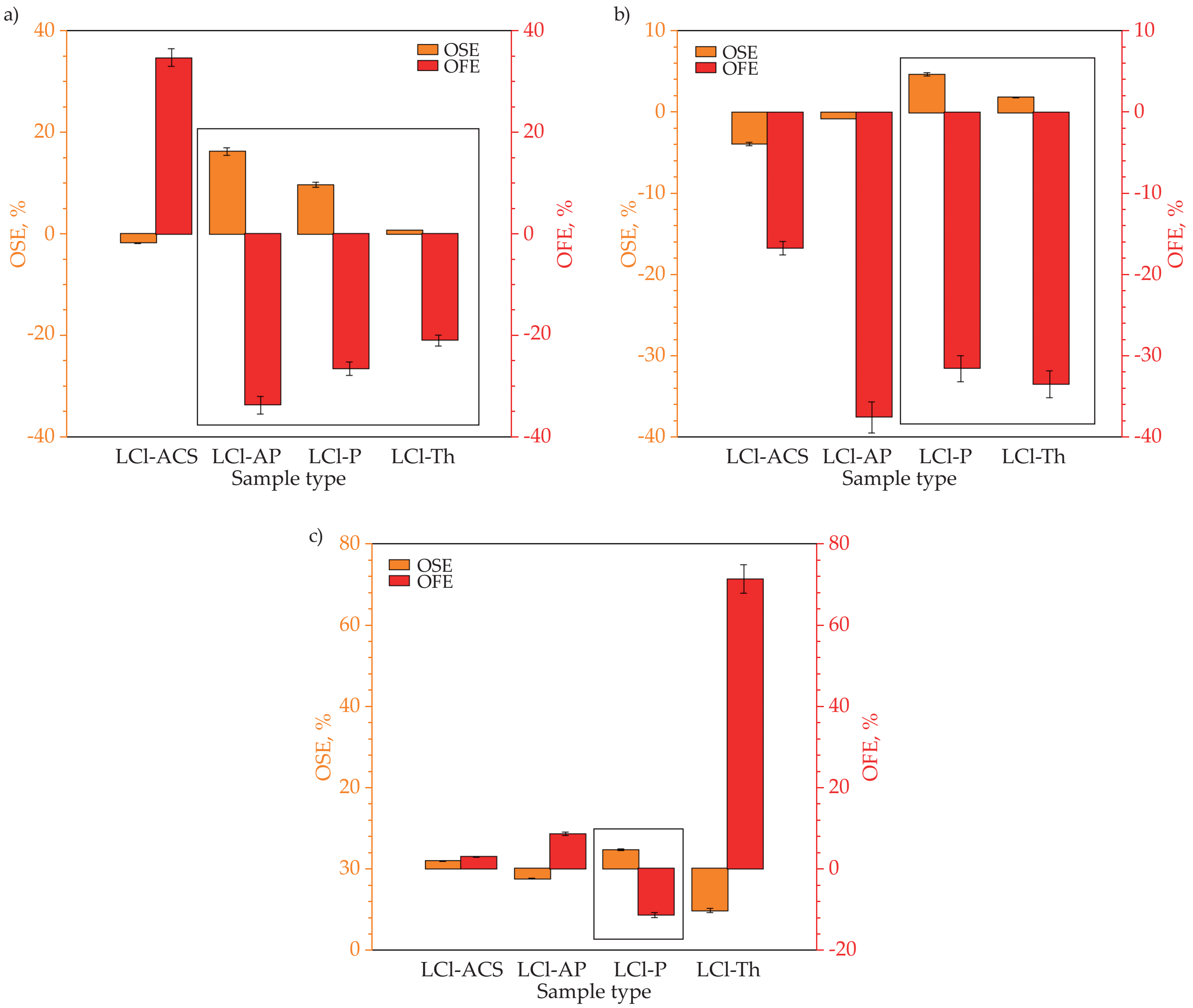

Fig. 5. Overall thermal stabilization effect (OSE) and overall flammability effect (OFE): a) DBAs, b) BDAs, c) DDAs

released is one of the most effective approaches to combustion blockers. The carbonaceous char formation reduces the amount of gaseous and condensed phases released and increases the amount of residue.

As shown in Figure 4, this relationship was met only by *N*-butyl-*N*-dodecyl-lignosulfonamides and didodecyl-lignosulfonamides obtained using methods B and C. However, flammability data excluded the use of didodecyl-lignosulfonamides and lignosulfonamides obtained according to reaction A2 (Table 3).

As assumed, only LCl-P-BDA and LCl-Th-BDA have good flame-retardant properties. To confirm this, the overall thermal stabilization effect (OSE) and the overall flammability effect (OFE) were determined using equations 1 and 2:

$$OSE = \sum_{T=423}^{873} [(\textit{mass percent of lignosulfonamide}_T) - (\textit{mass percent of lignosulfonate}_T)] \qquad (1)$$

$$OFE = \sum_{T=423}^{873} [(\textit{HRR percent of lignosulfonamide}_T) - (\textit{HRR percent of lignosulfonate}_T)] \qquad (2)$$

The obtained values of the OSE and OFE indicators relating to the CaL reference sample are summarized in Figure 5. In the case of DBAs, only the sample obtained according to reaction A2 did not show either improved thermal stability or reduced flammability compared to CaL. The best OFE and OSE indices were obtained for lignosulfonamides obtained according to reactions A1 and B. In the case of BDA, only two samples, obtained according to reactions B and C, met the OSE and OFE criteria at the same time. However, in the case of DDAs, only the sample obtained according to reaction B was characterized by both reduced flammability and improved thermal stability, considering the measurement area from 423 to 873 K.

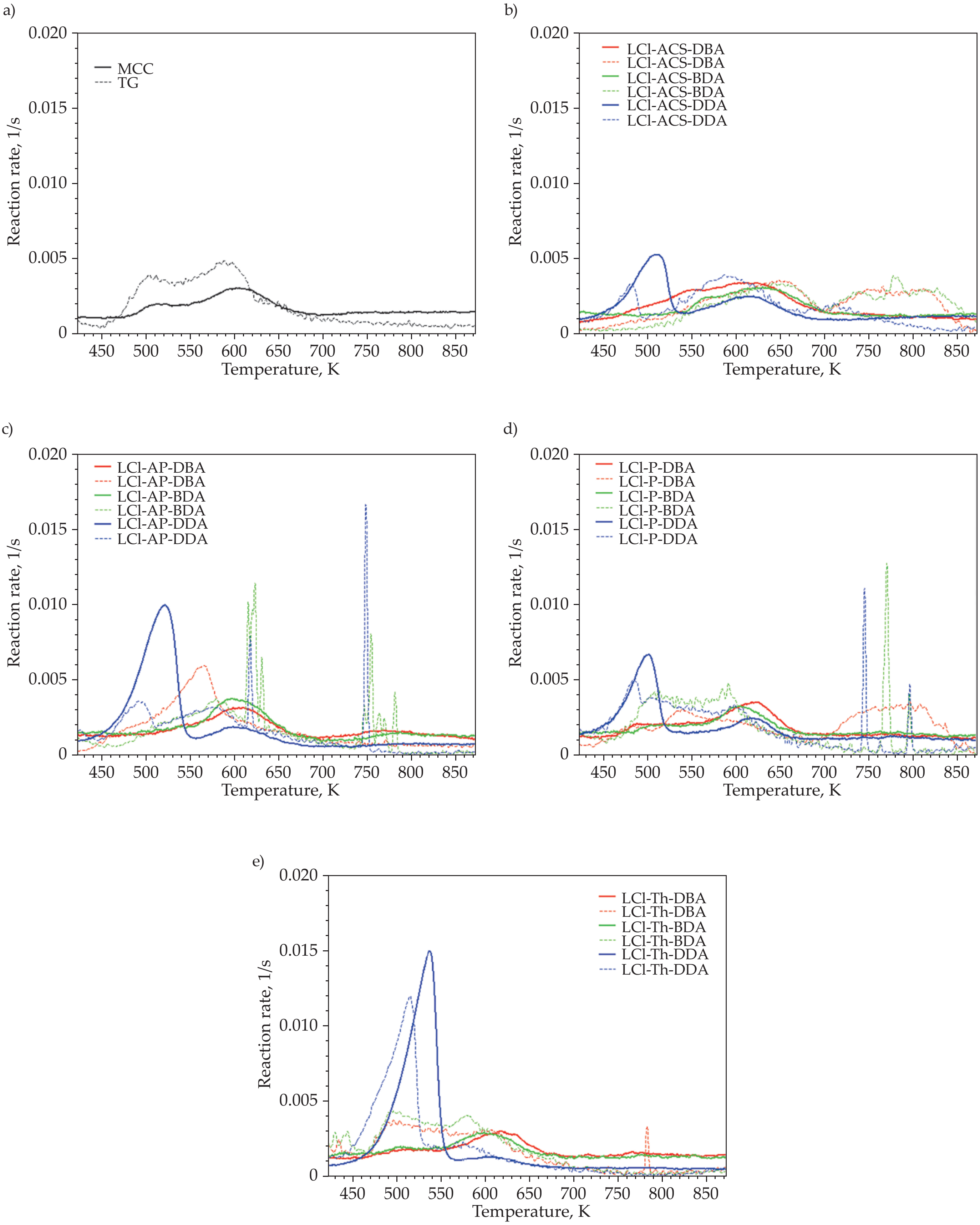

Fig. 6. Reaction rate for lignosulfonamides: a) reference sample, b) HCl and HSO_3Cl modification (ACS), c) HCl and PCl_5 modification (AP), d) PCl_5 modification (P), e) $SOCl_2$ modification (Th); thick solid line - reaction rate determined from MCC, thin dashed line - reaction rate determined from TGA

Figure 6 shows the decomposition reaction rates determined for the obtained lignosulfonamides based on the results of MCC and TG measurements. The results presented in Figure 6A for the reference sample are practically complementary. In turn, the curves illustrated for lignosulfonamides obtained according to reaction A2 (Figure 6B) indicate discrepancies only for DBAs and BDAs in the ranges above 700 K. Deviations in the reaction rate curves of the LCl-P-DBA sample were also observed to a similar extent (reaction B, Figure 6D). A common trend was observed for DBAs and BDAs, in which the reaction rate was dominant in the second stage of decomposition, i.e., in the range of 550–700 K. Conversely, DDAs decomposed very rapidly in the first stage of decomposition (400–550 K).

Moreover, samples modified with PCl_5 (reactions A1 and B) during TG analysis were characterized by a stepped character of the mass loss curve in the final phase of decomposition. This was due to the ability of these materials to undergo exothermic expansion when measured at temperatures above 700 K. In the reaction rate graphs, these anomalies are visible in the form of high and narrow peaks in the discussed measurement area.

CONCLUSIONS

Conditions for an effective method of synthesizing selected lignosulfonamides were developed. The combustion blocker itself emits energy of 0.67–6.75 kJ/g during combustion. For comparison, the heat of combustion of wood is 16–19 kJ/g, of hard coal 30 kJ/g of gasoline approx. 45 kJ/g, and of methane approx. 56 kJ/g. This means that these materials of natural origin are non-flammable. Moreover, the lignosulfonamides can increase the flame retardancy of biocomposite systems by optimizing the properties of the residual protective layer, adjusting the temperature range in which radical scavengers are released into the gas phase, or increasing the flame inhibition efficiency, i.e., they will slow down the combustion rate in the condensed phase and limit the flame in the gas phase. Promising results were obtained for LCl-P-BDA and LCl-Th-BDA. Also noteworthy are the samples LCl-AP-DBA, LCl-P-DBA and LCl-P-DDA. These three lignosulfonamides can be expected to act as effective synergists, tailoring a set of material properties to control the response of the sample in various fire behaviours, for example by regulating melt flow and dripping.

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