

Application of ion chromatography for determination of chlorine content in solid biomass for power sector

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Introduction

The technology for processing of biomass is based on physical, thermochemical and biochemical processes leading to the production of heat, electric power and biofuels [1]. Thermochemical process of biomass conversion is presented on Figure 1.

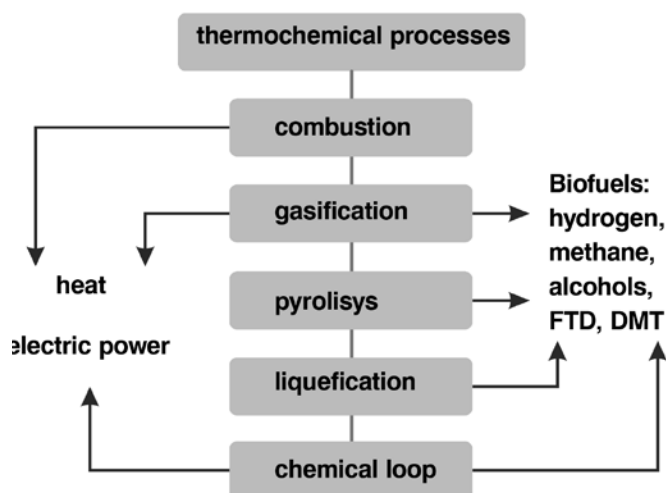


Fig. 1. Global technologies for biomass conversion [1]

One of the main parameters deciding whether particular type of biomass can be used in processes mentioned above is its chlorine content. Chlorine is present in plants mainly in form of chloride ion Cl^- and in low quantities as organic compounds. The percentage content of this element in biomass depends on the bioavailability of its compounds from air and soil. The crucial factor determining chlorine content in biomass is amount of chloride ions in soil solution, which depends both on natural occurrence of these ions in given soil and conducted agricultural treatments. Usually, mineral fertilizers are used in the form of salts, including chlorides, such as KCl . According to the literature data, the chlorine content in plants depends strongly on the type of biomass and varies between 0.005 and 2% weight of dry biomass. Wood biomass contains not more than 0.05% weight, while for annual plants such as cereal straw, corn, flax, rapeseed, grass, etc. it can be even up to 1% weight [2,3].

Long-term studies performed in Institute for Chemical Processing of Coal in Zabrze for the determination of physicochemical properties of biomass used in power sector, including chlorine content, have brought following results (Tab. I).

Chlorine together with nitrogen and sulphur is a major source of acidic compounds responsible for the corrosion of the installations and environmental pollution [2, 3, 4].

It is released in thermochemical processes from fuel as hydrochloride and molecular chlorine as a product of hydrochloride oxidation in combustion gas. These gases may cause corrosion in process installations. In the presence of alkali metals they cause slagging of heating surfaces of boiler and for fluidized bed boilers they may destabilise the bed due to local agglomerations [2, 4, 5]. Chlorine compounds have also strong effect on natural environment and living organisms. Both, HCl and Cl_2 are precursors for persistent

contaminants such as chlorophenols, PCBs (polychlorinated biphenyls), PCNs (polychlorinated naphthalenes), PCDDs (polychlorinated dibenzodioxins) and PCDFs (polychlorinated dibenzofurans) that have strong carcinogenic, mutagenic, teratogenic and sensitizing properties [6, 7, 8, 9, 10]. Moreover, these compounds coming with precipitation can contaminate soil and groundwater, causing their acidification, which also has negative effect on local ecosystems. Many different analytical methods are used for the determination of chlorine content in biomass, including titration, spectrometry, chromatography, X-Ray fluorescence (XRF) and high-temperature oxidizing combustion with electrochemical detection [7, 8, 10, 11].

Table I
Chlorine content in energy crops (biomass)

Biomass type	Chlorine content, % weight
Hay	0.220-0.354
Wood pellets	0.005-0.159
Willow	0.005-0.035
Straw	0.044-0.475
Corn	0.212-0.263
Miscanthus	0.053-0.158
PKS	0.005-0.105
Sunflower husk	0.061-0.229
Olive stones	0.289-0.981
Jerusalem artichoke	0.283-0.823
Rapeseed straw	0.295-0.713

The scope of this study is the determination of chlorine content using ion chromatography in biomass samples, including biomass used in power industry, in accordance with PN-EN 15289:2011 "Solid biofuels. Determination of total content of sulphur and chlorine". At the same, time obtained results were compared with chlorine contents determined by means of potentiometric titration with use of automatic titrator.

Materials and methods

Ion chromatography

Dionex ICS-5000 ion chromatography system equipped with EGC III KOH eluent generator, IonPac AS18 anion-exchange column, ASRS 300 suppressor and conductivity detector was used for tests. Calibration solutions were prepared using Fluka Primary Multi-anion Standard Solution and deionized water of 0.08 $\mu\text{S}/\text{cm}$ conductivity obtained from HLP5 system (Hydrolab, Poland).

Potentiometric titration

Biomass samples were combusted in IKA C5000 calorimeter. Chlorine content in actual samples and reference samples were determined using Crison Titromatic 1S automatic titrator equipped with ISE 5260 combination electrode.

Samples were prepared using deionized water of deionized water of 0.08 $\mu\text{S}/\text{cm}$ conductivity obtained from HLP5 system (Hydrolab, Poland) and such reagents as: silver nitrate (analytical grade; Chempur), potassium hydroxide (analytical grade; POCh) and industrial-grade oxygen (Linde-Gaz).

Principles of test methods

The samples were prepared in accordance with guidelines specified in European standard PN-EN 15289:2011 "Solid biofuels. Determination of total content of sulphur and chlorine". The chlorine content in the prepared solutions was subsequently determined using two different methods. In the first case, the determination was carried out in accordance with standard PN-EN ISO 10304-1:2009 "Water quality. Determination of dissolved anions by liquid chromatography of ions – part 1. Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulphate". In the second case, the chlorine content was determined by potentiometry using automatic titrator equipped with ISE 5260 combination electrode. The principles of chlorine determination are shown in diagrams (Figs. 2 and 3).

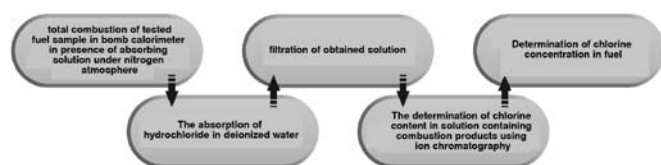


Fig. 2. Procedure diagram of analysis using ion chromatography

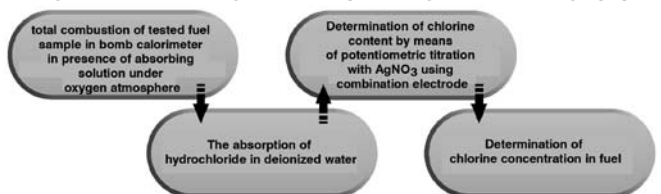


Fig. 3. Procedure diagram of analysis using potentiometric titration

Determination of chlorine content in blank control was carried out using both methods and by applying mineralization procedure without biomass sample. If it is assumed that total chlorine present in the fuel passes to solution as Cl^- anions, its content in analysed fuel may be calculated by using following formulas:

For chromatography:

$$Cl^a = \frac{V \times (C - C_0)}{m} \times 100\% \quad (1)$$

where:

Cl^a – chlorine content in biomass test sample, % weight

C – chlorine concentration in absorption solution determined by ion chromatography, mg/l

C_0 – chlorine concentration in absorption solution determined by ion chromatography for blank control, mg/l

V – total volume of absorption solution after dilution, ml

m – biomass sample weight, mg

For titration:

$$Cl^a = \frac{(V_1 - V_0) \times 0,0008865 \times V_2}{m \times V_3} \times 100\% \quad (2)$$

where:

Cl^a – chlorine content in biomass test sample, % weight

V_0 – volume of silver nitrate (V) standard solution used for titration of Cl^- ions in blank control equivalent to 0.025 mol/l solution, ml

V_1 – volume of silver nitrate (V) standard solution used for titration of Cl^- ions in solution containing products of biomass sample combustion equivalent to 0.025 mol/l solution, ml

V_2 – total volume of solution obtained from combustion of biomass sample, ml

V_3 – volume of solution obtained from combustion of biomass sample, used for determination, ml

m – biomass sample weight, g

Tested material

Following samples were analysed:

- Certified reference materials (CRM): Ziola Polskie (Polish herbs) INCT-MPH-2, Liście Herbaty (Tea leaves) INCT-TL-1; (Institute of Nuclear Chemistry and Technology, Analytical Chemistry Department)
- reference materials (RM): Grass (mixture) IPE-952, Conifers IPE-879, Wheat (straw) IPE-881; (Wepal)
- various biomasses.: stalk of Jerusalem artichoke, olive bagasse, hay pellet, wood pellet, willow, PKS, sunflower husks, roasted grain coffee waste pellet, separatino, acai berry pits, bamboo, miscanthus, wood chips, corn chips, pine, rose, beet bagasse and fruit bagasse pellet, lignin pellets, hydrolysed wood, conifers

Determination of validation parameters

In order to determine selectivity factor of determination method of chlorine content in biomass using ion chromatography, the standard solution Primary Multianion Standard Solution and biomass sample were analysed.

Based on the analyses of standard solution that contain F^- , Cl^- , Br^- , NO_3^- , PO_4^{3-} , SO_4^{2-} (Fig. 5) the retention time of chloride ion was determined ($4.72 \pm 0,01$ min).

Figures 4 and 5 show example chromatograms registered for standard solution and for solution of tested sample under following conditions:

- guard column – Dionex IonPac AG 18
- analytical column – Dionex IonPac AS 18
- temperature 30°C
- eluent: 23 mM KOH
- eluent flow rate 0.25 ml/min, isocratic flow
- dispensed sample volume 10 μl
- conductivity detector.

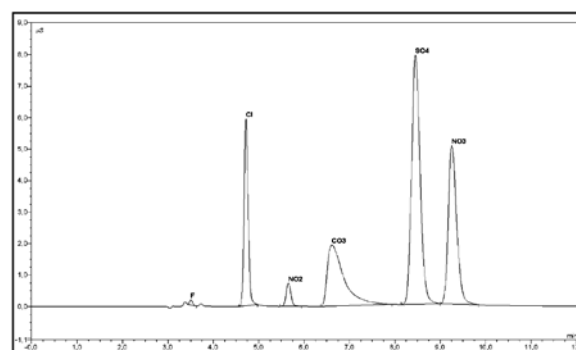


Fig. 4. Anions chromatogram in biomass sample

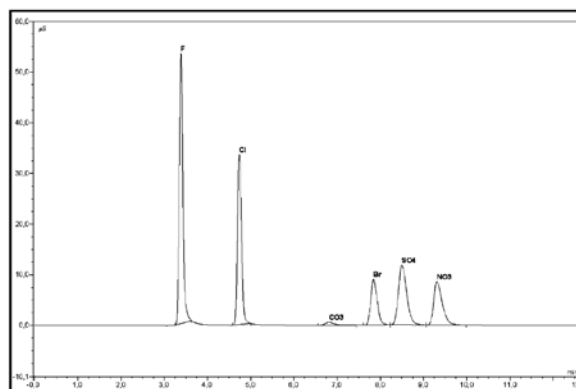


Fig. 5. Anions chromatogram in anion mixture standard solution Primary Multianion Standard Solution

In order to determine linearity of the method, series of standard solutions containing chloride ion in concentration range from 0.1 mg/l to 10.0 mg/l. The calibration curves for chlorine content determination in biomass were prepared based on obtained results (Figs. 6 and 7).

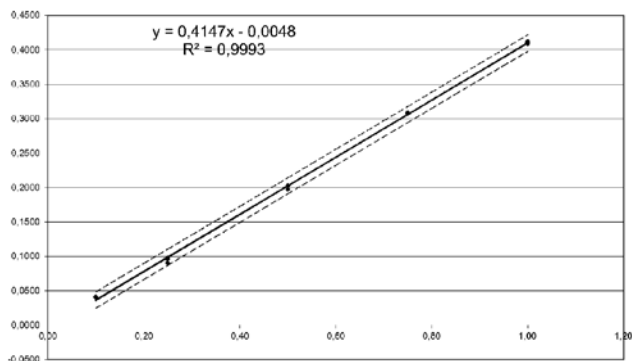


Fig. 6. Calibration curve for chloride ions in concentration range from 0.1 mg/l to 1.0 mg/l

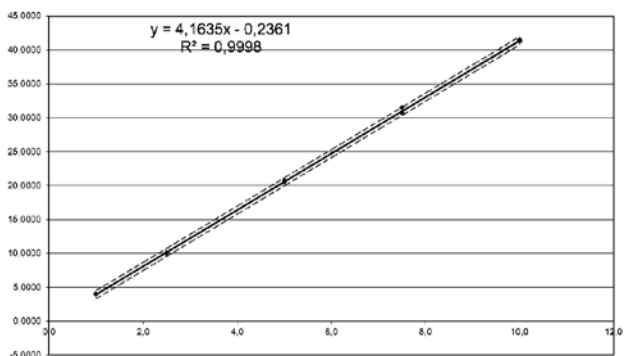


Fig. 7. Calibration curve for chloride ions in concentration range from 1.0 mg/l to 10.0 mg/l

Calculated correlation coefficient (R^2) and slope (a) for curve in range from 0.1 mg/l to 1.0 mg/l were 0.9993 and 0.4147, respectively, while for curve in range from 1.0 mg/l to 10.0 mg/l were 0.9998 and 4.1635, respectively. The correlation coefficients meet assumed acceptance criterion ($R^2 \geq 0.9990$).

The LOD (limit of detection) and LOQ (limit of quantification) were estimated based on the analysis of blank control. Their values are 0.001% and 0.004%, respectively.

Actual samples of energy crops (biomass) were used for the determination of repeatability of analytic method. Four different types of biomass of different levels of chlorine content were selected. For each level, 4 series of tests were carried out, 8 measurements each. The repeatability was determined as arithmetic mean of calculated variation coefficient for each of series. Tables 1 ÷ 4 show obtained results, for each level together with variation coefficient for each series and mean variation coefficient for given level. The repeatability of the analytic method was determined using propagation law and considering mean values of variation coefficient for each level. The value of repeatability is 5%.

Table 2
Measurement results for biomass samples obtained in conditions of repeatability and intermediate precision for level 1

Series number	Level 1			
	Series 1	Series 2	Series 3	Series 4
Measurement 1	0.015	0.014	0.015	0.0142
Measurement 2	0.014	0.014	0.014	0.0138
Measurement 3	0.015	0.014	0.015	0.0149
Measurement 4	0.015	0.014	0.014	0.0137
Measurement 5	0.015	0.014	0.014	0.0135
Measurement 6	0.015	0.013	0.014	0.0142
Measurement 7	0.014	0.014	0.013	0.0148
Measurement 8	0.015	0.014	0.015	0.0140
Variation coefficient, %	3.0	3.0	4.2	3.5
Mean variation coefficient	3.5			

Table 3
Measurement results for biomass samples obtained in conditions of repeatability and intermediate precision for level 2

Series number	Level 2			
	Series 1	Series 2	Series 3	Series 4
Measurement 1	0.120	0.126	0.116	0.120
Measurement 2	0.125	0.121	0.120	0.118
Measurement 3	0.124	0.122	0.118	0.114
Measurement 4	0.113	0.128	0.117	0.121
Measurement 5	0.119	0.121	0.118	0.124
Measurement 6	0.121	0.117	0.113	0.116
Measurement 7	0.119	0.129	0.123	0.118
Measurement 8	0.123	0.124	0.121	0.121
Variation coefficient, %	3.1	3.3	2.6	2.7
Mean Variation coefficient	2.9			

Table 4
Measurement results for biomass samples obtained in conditions of repeatability and intermediate precision for level 3

Series number	Level 3			
	Series 1	Series 2	Series 3	Series 4
Measurement 1	0.454	0.462	0.456	0.466
Measurement 2	0.453	0.449	0.453	0.452
Measurement 3	0.456	0.468	0.467	0.459
Measurement 4	0.447	0.462	0.459	0.452
Measurement 5	0.451	0.458	0.459	0.453
Measurement 6	0.449	0.457	0.460	0.454
Measurement 7	0.459	0.455	0.453	0.457
Measurement 8	0.449	0.462	0.460	0.469
Variation coefficient, %	0.9	1.2	1.0	1.4
Mean Variation coefficient, %	1.1			

Table 5
Measurement results for biomass samples obtained in conditions of repeatability and intermediate precision for level 4

Series number	Level 4			
	Series 1	Series 2	Series 3	Series 4
Measurement 1	0.797	0.789	0.796	0.801
Measurement 2	0.795	0.792	0.789	0.812
Measurement 3	0.789	0.799	0.783	0.800
Measurement 4	0.822	0.816	0.790	0.796
Measurement 5	0.796	0.810	0.802	0.723
Measurement 6	0.799	0.814	0.806	0.788
Measurement 7	0.791	0.809	0.776	0.792
Measurement 8	0.802	0.794	0.793	0.794
Variation coefficient, %	1.3	1.3	1.2	3.5
Mean Variation coefficient, %	1.8			

Based on the results presented in Tables 1 ÷ 5 the value of intermediate precision for each level was calculated. Following values were obtained: for level 1 – 4.0%, for level 2 – 3.3%, for level 3 – 1.3%, for level 4 – 2.1%. The value of intermediate precision of analytic method was calculated using propagation law and it is 5.7%.

The correctness of the method [12] was determined based on use of series of certified and reference materials. The results are presented in Table 6.

Table 6

Accuracy and correctness of chromatographic method

Sample	Chlorine content in reference material.	Chlorine content determined as mean from six repeated measurements	Correctness. %
	%	%	
INCT-MPH-2	0.284±0.002	0.298±0.020	104.9±9.7
INCT-TL-1	0.0573±0.0048	0.0556±0.0040	97.0±12.0
IPE-952	0.623±0.009	0.604±0.014	97.0±8.3
IPE-879	0.477±0.013	0.463±0.007	97.1±3.2
IPE-881	0.116±0.007	0.118±0.003	101.3±6.4

The calculated values of correctness meet acceptance criterion, i.e. they are in range 80% - 120%.

The comparison between ion chromatography and potentiometric titration was based on validation parameters, i.e. correctness and precision. Precision of both methods was compared using Snedecor's F-test. Based on the calculated value of Snedecor's F-test, it was concluded that titration method differs in precision from ion chromatography with statistical significance. Table 7 presents results of comparison between analytic methods.

Table 7

Comparison of precision of analytic methods

	Chromatography	Titration
Results, %	0.015	0.020
	0.014	0.018
	0.015	0.016
	0.015	0.019
	0.015	0.012
	0.015	0.010
	0.014	0.012
	0.015	0.014
Mean	0.015	0.015
Standard deviation	0.441·10 ⁻³	0.004
Value of Snedecor's F-Test	68.01	
Critical value for Snedecor's F-Test	3.79	

The comparison of methods' accuracy was carried out using Cochran and Cox test because compared methods have different precision. Calculated statistic of test is 2.713 and is higher than critical value, i.e. 2.365. That means the difference in accuracy between methods is statistically relevant (Tab. 8).

Table 8

Cochran-Cox test results

	Chromatography	Titration
Results	0.015	0.020
	0.014	0.018
	0.015	0.016
	0.015	0.019
	0.015	0.012
	0.015	0.010
	0.014	0.012
	0.015	0.014
Mean	0.015	0.015
Standard deviation	0.441·10 ⁻³	0.003
Z-test value	2.85·10 ⁻⁹	1.94·10 ⁻⁶
C-test value	2.713	
Critical value	2.365	

Performed tests have given chlorine content in samples of different types of biomass, including biomass used in power sector, using ion chromatography. The results are presented in Figure 8.

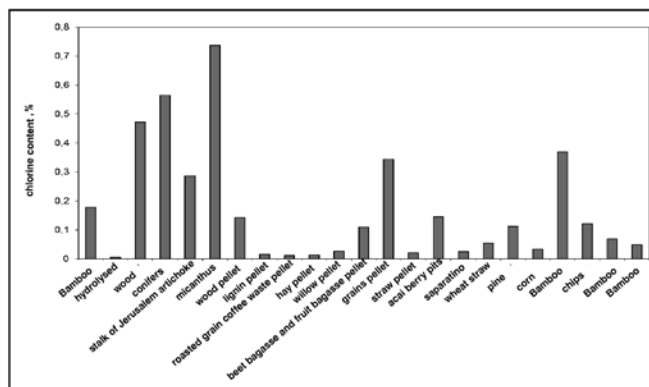


Fig. 8. Chlorine content in different types of biomass

Figure 9 shows results of chlorine content determination for exemplary samples of biomass of concentration level from 0.005 to 0.123% weight obtained using discussed methods.

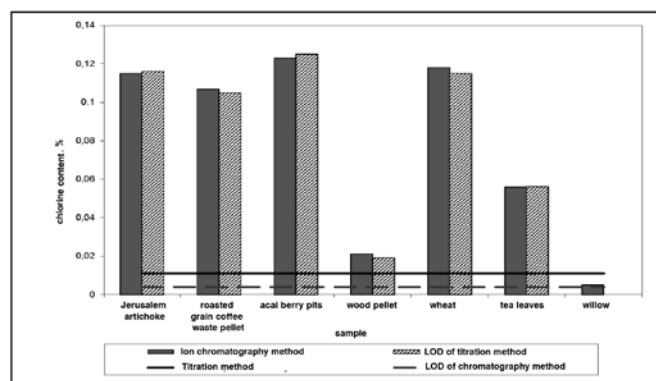


Fig. 9. Chlorine content in biomass samples

Due to the higher sensitivity of chromatographic method in comparison with titration, it was possible to determine chlorine content in sample of willow, i.e. 0.005 % weight .

Summary and conclusions

The availability of new, automated analytic techniques facilitates and improves lab work. Modern solutions allow determination of tested analyte with much higher accuracy. Moreover, due to the higher sensitivity of modern instruments it is possible to determine low contents of analyte. The application of ion chromatography method for determination of chlorine content in energy crops (biomass) creates the possibility to determine chlorine content in broad range of concentrations. The determined content in biomass sample varied in range from 0.005% weight for willow and to 0.738% weight for stalk of Jerusalem artichoke. The optimum condition for separation is possible due to the high selectivity of the method, which allows to determine several different elements present in the fuel at the same time.

The repeatability of the method is 5%, while its intermediate precision is 6%. The correctness determined for different levels meet acceptance criterion, i.e. is in range 80%-120%. LOQ for ion chromatography is 0.004 % weight and is much closer to LOD, which is equal to 0.011% weight .

Statistical tests have shown differences of precision and accuracy between compared methods. Ion chromatography is more accurate. Moreover, calculated values of Snedecor's F-test show that titration is less precise than chromatographic method.

Value of LOQ, costs and time required for single analysis, as well as ease of its execution are major factors taken into account while choosing given analytic method.

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LOTOS i Grupa Azoty zainwestują 12 mld PLN w polską petrochemię

3 grudnia 2013 r. Grupa LOTOS SA i Grupa Azoty SA podpisały porozumienie w sprawie powołania spółki celowej i wykonania pełnego studium wykonalności kompleksu petrochemicznego, zlokalizowanego przy obecnych instalacjach LOTOSU i Grupy Azoty.

Obie firmy podpisały też wstępne porozumienie z Polskimi Inwestycjami Rozwojowymi, jako potencjalnym inwestorem finansowym przy realizacji ww. przedsięwzięcia. Wartość inwestycji szacowana jest na ok. 12 mld PLN, co będzie oznaczało rekordową inwestycję w polskim przemyśle w ostatnich latach. Jej realizacja pozwoli na obniżenie deficytu Polski w handlu chemikaliami, a także zapewni 5–7 tys. miejsc pracy w okresie budowy instalacji i ok. 2 tys. po oddaniu ich do użytku. Koszty (związane z przygotowaniem studium wykonalności i działalnością ww. spółki) poniesie w równych częściach Grupa LOTOS i Grupa Azoty. Zgodnie z zapisami odrębnego porozumienia Polskie Inwestycje Rozwojowe będą wspierać konsorcjum merytorycznie w kwestiach strukturyzacji finansowej i kontraktowej projektu.

Po przeprowadzeniu studium wykonalności, podjęcie decyzji inwestycyjnej planowane jest na 2014 r. W przypadku pozytywnej decyzji inwestycyjnej i ustrukturyzowaniu finansowania, budowa kompleksu będzie trwała od 2016 do 2018, a jego uruchomienie może nastąpić w 2019 r. (em)

(Informacja prasowa LOTOS, 3 grudnia 2013 r.)

Lanxess rozszerza produkcję krezoli

Firma Lanxess ukończyła rozbudowę zakładu produkcji krezoli w Leverkusen (Niemcy). Inwestycja obejmowała budowę nowego obiektu do przeprowadzania reakcji oraz drugiej, 46-metrowej kolumny destylacyjnej. Dzięki rozbudowie zakład zwiększy o jedną piątą zdolności produkcyjne substancji stosowanych m.in. w przemyśle środków agrochemicznych oraz do produkcji witaminy E, aromatów, żywic i środków opóźniających palność. Budowa nowych obiektów trwała niemal półtora roku i kosztowała ok. 20 mln EUR. (kk)

(<http://www.plastech.pl>, 22.11.2013)

Abengoa wprowadza nowy projekt produkcji biopaliw II generacji

Jeden z największych producentów biopaliw, Abengoa planuje budowę fabryki biopaliwa kolejnej generacji w porcie w Seville. Instalacja ma posiadać moce produkcyjne na poziomie 28 mln litrów rocznie i kosztować ok. 120 mln EUR. Abengoa obecnie posiada kilkanaście fabryk konwencjonalnego etanolu na terenie Hiszpanii, USA, Holandii oraz Brazylii. Dodatkowo jedną fabrykę biodiesla w Hiszpanii. Dotychczasowe działania firmy w zakresie biopaliw kolejnych generacji skupiały się na produkcji etanolu celulozowego w Balbilarfuentes w Hiszpanii (działająca już od 2009 r.), na instalacji demonstracyjnej w York, Nebraska w USA (działająca od 2007 r.) oraz w Hugoton, Kanadzie (uruchomiona w ciągu najbliższych miesięcy). Ponadto, w zeszłym roku uruchomiono produkcję na małą skalę biopaliw, bazujących na algach w Kartagenie w Hiszpanii. (kk)

(<http://www.e-biopaliwa.pl>, 13.11.2013)

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