From "Sirups" to Biocarbons. A 30-Year Cooperation Research for Better Biomass Utilization with Michael J. Antal, Jr.

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ABSTRACT. The results of a 30-year US – Hungarian research cooperation are surveyed. The head of the cooperating US laboratory, Michael J. Antal, Jr., deceased on 21 October 2015. He was a leading person in biomass research. The collaboration started with pyrolysis studies. In this phase of the work the aim was to clarify the factors that enhance the formation of the valuable volatile products ("sirups"). For this purpose the kinetics and mechanism of the biomass pyrolysis was studied with a particular emphasis on the behavior of the cellulose component. Later the interest of the cooperation gradually shifted to the solid products of the pyrolysis: chars, charcoals and biocarbons. Hence the formation, properties and uses of these products were studied. The present article illustrates the three decades of the common work by selected results. Such examples are shown which are thought (i) to be useful in the planning of future studies on pyrolysis and combustion of biomass materials; (ii) and/or may help in the interpretation of the existing literature data. The presented results include the choice of the proper experimental conditions; the evaluation of experiments with linear and non-linear temperature programs by the method of least squares; the assessment of complex mechanism schemes by suitable series of experiments; and the kinetic modelling of the combustion of inhomogeneous chars in the kinetic regime.

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1. INTRODUCTION

This paper surveys a long-time cooperation between a US and a Hungarian laboratory. Such examples are shown from the results which are thought to be relevant to the present day biomass R&D activities.

The cooperation started in 1984, when Michael J. Antal, Jr., a distinguished professor of the University of Hawaii, visited our laboratory in Budapest and lasted until his death on October 21, 2015. In this paper we shall refer to him as MJA, an abbreviation that he, himself used regularly. In 1984 MJA was already a well-known expert in biomass research and a pioneer in the field. His first biomass paper appeared in 1976 about the production of fuel from biomass and other wastes by solar energy.[1] Two years before this trip to Hungary he published a comprehensive critical review on the pyrolysis of carbohydrate biomasses[2] where he dealt with the nomenclature, too, introducing the term *sirups* as follows: "Sirups are commonly referred to as 'tars' in the literature, but this use of the word tars is misleading. Tars are composed of hydrocarbons, whereas the sirups are composed of anhydrosugars and related carbohydrates. The spelling of the 'sirups' was chosen to differentiate the pyrolysis products from edible syrups." The term *sirups* was accepted by other investigators, too.[3]

The Hungarian side had two specialties that were used later in this cooperation. The first was a sensitive, computerized thermobalance – mass spectrometer system (TGA – MS).[4,5] The system was equipped by an in-house developed data processing software that carried out base line corrections, normalizations and produced graphics on the mass spectrometric intensities, sample mass and mass loss rate as functions of time or temperature. Beside the TGA-MS, a pyrolysis GC-MS system was also used in the study of thermal reactions.[5]

A further specialty was an algorithm and software for the kinetic evaluation of non-isothermal experiments. This method, published in 1979, allowed the simultaneous least squares evaluation of more than one non-isothermal experiment at any sort of temperature programs.[6] The following objective function was minimized numerically:

$$of = \sum_{k=1}^{N_{exper}} \sum_{i=1}^{N_{points}} \left[X_k^{obs}(t_i) - X_k^{calc}(t_i) \right]^2 \tag{1}$$

Here X_k^{obs} is an experimental quantity normalized by the initial sample mass: DSC signal or TGA signal (m) or mass loss rate (-dm/dt). Subscript k distinguishes the experiments evaluated together. X_k^{calc} denotes the predicted values of the *k*th experimental curve which is obtained by the numerical solution of the kinetic equation at each iteration step. N_{points} denotes the number of t_i time points at which a digitized value is available. N_{exper} is the number of experimental curves evaluated together. The capabilities of the method were demonstrated by the simultaneous evaluation of two simulated "experiments".[6] These simulated experiments were reconstructed for the present article using the parameters published in 1979. (See Figure 1). After the start of the common work with MJA, the method was implemented to personal computers and was used for more complex kinetic models, too.[7] When experiments with highly differing

magnitudes were evaluated together, the $X_k^{obs} - X_k^{calc}$ differences were normalized by the highest X_k^{obs} value of the given experiment.[8] Besides, a division by N_{points} became also necessary in eq 1 because the number of digitized points varied from experiment to experiment.
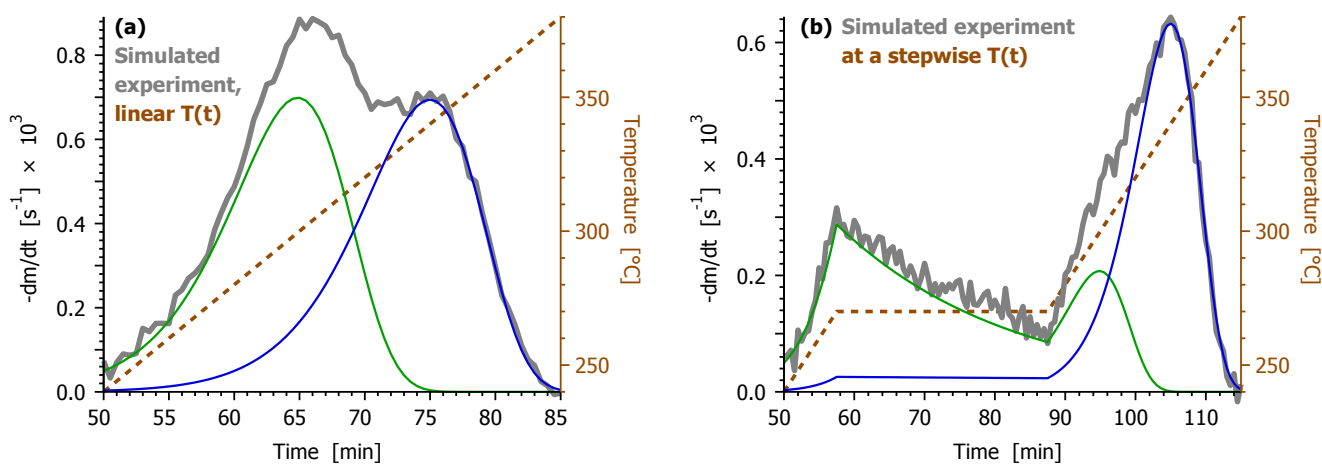

Figure 1. Simulated experiments which were evaluated simultaneously by the method of least squares as a test in 1978.[6] Dashed brown lines show the *T(t)* functions at which the experiments were simulated. The green and blue lines represent the mass loss rate of first order reactions. The thick gray lines were constructed by adding a Gaussian noise of $\sigma = 1.67 \times 10^{-3}$ s^{-1} (0.10 min^{-1}) to the sum of the green and blue curves.

The first part of the cooperation aimed at a better understanding the effects that influence the course of the pyrolysis. In that time the volatile products were thought to be the most desirable. The word "sirups" in the title expresses this opinion. As the work proceeded, MJA's attention gradually turned in the direction of the solid pyrolysis product: to chars, charcoals and biocarbons. We investigated the pyrolysis processes in further works, too, but the goals shifted to a better understanding the char formation. Later we studied the properties and the possible uses of the various biochars and biocarbons that were produced in Hawaii by the methods developed by MJA and his coworkers.

Most of the researches surveyed in the present article were carried out by thermal analysis methods: thermogravimetric analysis (TGA), thermogravimetry − mass spectrometry (TGA-MS), and differential scanning calorimetry (DSC). Due to their precision and well-controlled experimental conditions, these techniques are useful tools in biomass research. However, they can be employed only at relatively low heating rates because the true temperature of the samples becomes unknown at high heating rates. Accordingly their results cannot be utilized directly in the modeling of industrial processes that include high rate heating.

The papers with the authorship of MJA received more than 10,600 citations.[9] Around a quarter of these citations were received for the articles of the collaboration surveyed in the present article.[9] Part of the

work, especially in the last few years, were carried out as a US – Norwegian – Hungarian trilateral cooperation in which MJA participated till his very last days. The latest common article was published recently.[10]

Figures 2 and 3 show MJA with cooperation partners at the beginning and at the end of the cooperation work.

Figure 2. July 1986 in Budapest, in the laboratory of the Hungarian Academy of Sciences. Back row, from left to right: Michael J. Antal, Jr., a technician (Linda Nemes), and Gábor Várhegyi. Front row: Piroska Szabó (left) and Emma Jakab (right), authors in several articles of the cooperation. Equipment in the background: the mass spectrometer and the computer of the TGA-MS system
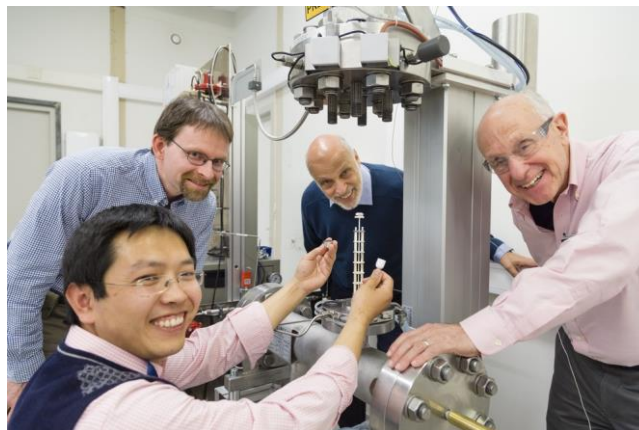
Figure 3. April 2014 in Trondheim, Norway, in the laboratory of SINTEF Energy.[11] From left to right Liang Wang, Øyvind Skreiberg, Gábor Várhegyi and Michael J. Antal, Jr. The equipment in the photo is a high-pressure TGA. (Photographer: Thor Nielsen.[11])

2. BIOMASS PYROLYSIS

2.1 TGA-MS Studies on the Pyrolysis of Cellulose, Hemicellulose and Sugar Cane Bagasse. The collaboration started by the TGA-MS examination of two biomass components and an important agricultural byproduct: a cellulose (Avicel);[12] a representative hemicellulose [(4-O-methyl-D-glucurono)-D-xylan];[13] and a sugar cane bagasse sample.[14] In these works we elaborated the interpretation of the TGA-MS experiments of the biomass plant materials via the comparison of the mass loss rate curves and the time/temperature dependence of the mass spectrometric intensity curves. A particular emphasis was made on the catalytic effects of a few low-cost inorganic materials.[12,14] Such compounds were chosen (NaCl, $MgCl_2$, $FeSO_4$ and $ZnCl_2$) of which one could assume practical applicability in potential industrial processes. Besides, the effect of the secondary reactions were also studied in TGA under well-defined conditions. For this purpose the samples were put into sealed vessels where only a pinhole on the top allowed the leave of the formed volatiles. The char yield of Avicel increased from 5% to 19% (m/m, db) in this way, which was explained by the secondary char formation from the tars. The mass spectrometric fragments clearly indicated the secondary reactions of the tars.

The effect of a long isothermal preheating at 260°C was also studied for the cellulose and bagasse samples. This part of the work aimed at a better understanding of the first steps of the cellulose decomposition. The corresponding experiments on bagasse may be regarded as a simple study of a torrefaction process under well-defined conditions. (Though we did not recognize the significance of this technology that time and did not use the term "torrefaction".) Figure 4 shows the corresponding results. The peaks are magnified to an equal height for a better comparison. The preheating caused only negligible effect on the Avicel pyrolysis. The shape and width of the mass loss rate peak did not change while the 2°C temperature difference in the peak temperatures is negligible. Most of the hemicellulose

content of the bagasse decomposed during the preheating, as it could be expected. This was indicated by the lack of the side peak around 315°C. It is interesting that the preheating shifted the cellulose decomposition to somewhat higher temperatures in that case, as shown in Figure 4b.
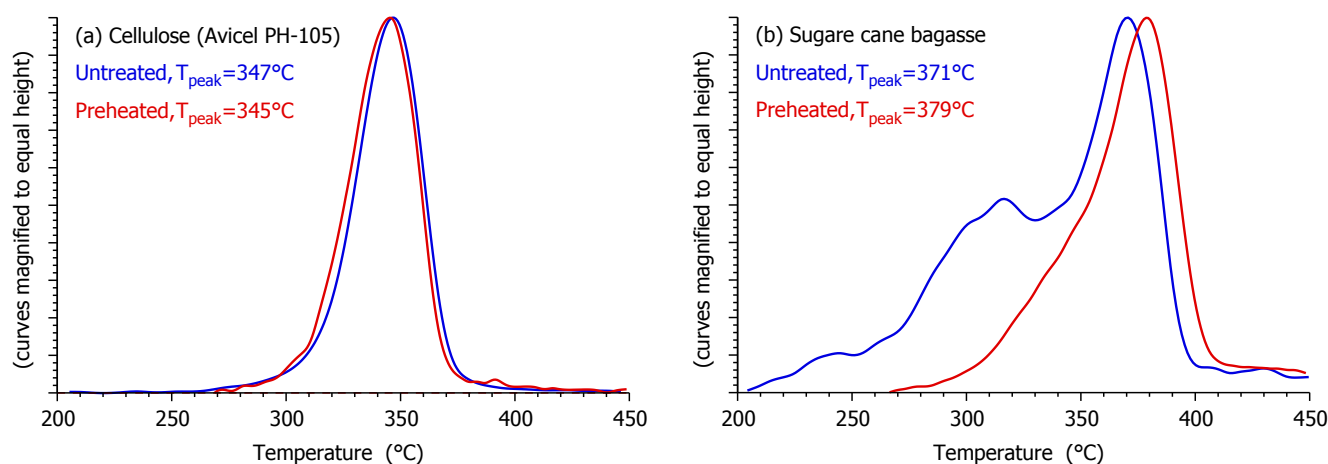

Figure 4. Effect of a 2-hour preheating at 260°C on the pyrolysis of cellulose (a) and bagasse (b).[12,14] (The experiments, carried out in 1986, were reprocessed for the present work.)

2.2. On the Validity of the Broido-Shafizadeh models for Cellulose Pyrolysis. In a later work[15] more experiments were carried out on Avicel cellulose employing a wider range of heating programs. The validity of the Broido-Shafizadeh model was examined, which was based on the following reaction schemes:
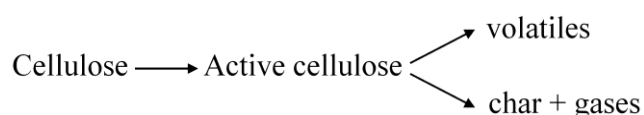
Reaction Scheme 1: The Bradbury, Sakai, and Shafizadeh model for cellulose pyrolysis[16]

Here the first reaction is not accompanied by any mass loss hence it is not detectable by TGA. At lower temperatures the lower branch is dominant (Active cellulose $\rightarrow$ char + gases), while at higher temperatures the active cellulose decomposes mainly to volatiles. Reaction Scheme 1 is a simplified version of an earlier, more detailed scheme (see Reaction Scheme 2) which was established by Broido.[17]

"A"———>"B"———┬———> volatile "tars"
             │
             └——> "C" +... ———> "D" +... ———> "E" +...
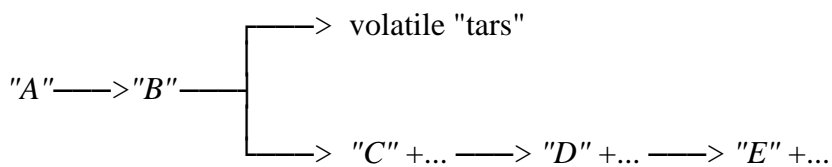
Reaction Scheme 2: The multistep model of Boido for cellulose pyrolysis[17] Notation: "A" is cellulose, "B" is active cellulose, "C" and "D" are solid intermediate products, "E" is the final char, and the ellipses stand for volatile products.

We tested the validity Reaction Scheme 2 by a further TGA study. Figure 5 shows the temperature programs employed. The corresponding system of differential equations were solved along the given $T(t)$ functions. (See Varhegyi et al.[15] for the details.) The most important conclusion of the work was: "The cellulose → active cellulose step of the Broido-Shafizadeh model is superfluous within the temperature range 250-370 °C. Experimental results are better represented by models which exclude this reaction." Obviously this does not exclude the presence of an initial cellulose → active cellulose reaction. Our results show only that this reaction, if takes place, is not rate determining. For example one can imagine that its reaction rate becomes high at the temperatures where the cellulose decomposition has measurable mass loss rates. If so then the rate determining step is another reaction in the scheme.
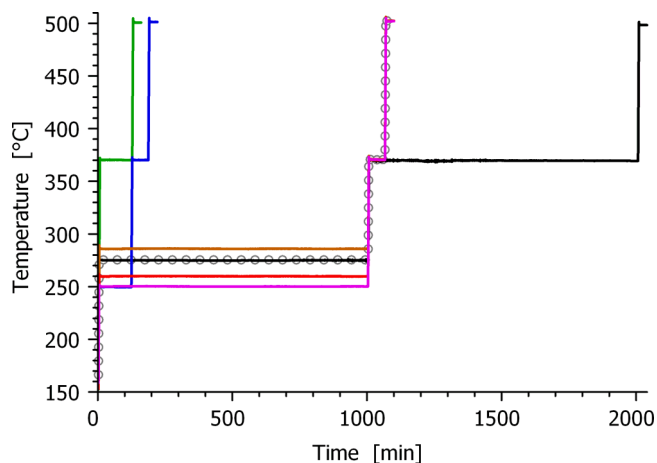

Figure 5. Nine temperature programs employed to test the validity of the Broido reaction scheme. The heating rate in the non-isothermal sections was 40°C/min. See Várhegyi et al.[15] for the durations and temperatures of the isothermal sections. Each $T(t)$ program is represented by a different color. The magenta line covers the red and dark orange lines from $t \cong 1004$ min until the end of these programs. The $T(t)$ programs represented by gray circles and solid black lines differ only in the length of the second isothermal section. The heating below 150°C is not shown in this figure; it was the same for all experiments (40°C/min).

The reliability of the works that led to the introduction of the cellulose → active cellulose reaction step[16-18] was also examined. We found that these works could not be regarded as a dependable proof for the importance of the cellulose → active cellulose in mass loss rate kinetics. Among others, Broido et al.[17,18] employed comparatively large (90 mg) samples while Bradbury et al.[16] worked with 250 mg samples. Diffusion effects and the secondary reaction of the volatiles could occur in both cases. Besides, heat transfer problems probably also arose in the work of Bradbury et al.[16] In addition, it was not possible to examine numerically the necessity for a given reaction step in a complex reaction network in the seventies because the sufficient hardware and software were not available for these studies.

From the middle of the nineties MJA's interests turned gradually to other directions and we abandoned the joint research on the kinetics and mechanism of the cellulose pyrolysis. Nevertheless, I participated in other biomass pyrolysis studies, outside of this cooperation. We examined a wide variety of lignocellulosic samples with linear, stepwise, modulated and constant-reaction-rate temperature programs.[19,20] The cellulose → active cellulose step was not needed for the description of the cellulose kinetics in the models.

2.3. The Reliability of the TGA experiments. In a series of further works with MJA we studied the reliability of the TGA experiments.[21-23] The results obtained in this direction may be useful nowadays, too, in the assessment of the existing literature as well as in the planning of new experiments. An example is shown in Figure 6, which illustrates how important is the choice of small sample masses for the experiments.[22] The curves plotted by blue and red colors in Figure 6 belong to TGA experiments at heating rate 65°C/min. The sample mass differs, however: it was 0.30 mg at the blue curves, and 9.2 mg at the red curves. The alteration in the measured peak temperatures was nearly 40°C and the width of the -dm/dT curves also differ. This effect is a typical example for a large thermal lag: the sample is cooler than the temperature measured by the thermocouple of the equipment. (Diffusion problems cannot cause such effect on cellulose because the cellulose pyrolysis is catalyzed by the formed volatiles, especially by the formed H_2O. This phenomena will be outlined in the next section. If the escape of the products is delayed, the larger organic product molecules undergo secondary reactions inside the sample and the forming H_2O catalyzes the cellulose pyrolysis.) Note that the endothermic reaction heat of the biomass pyrolysis is not particularly high. Mok and Antal measured values below 0.24 kJ/g for cellulose pyrolysis.[24] On the other hand, the combustion heat of the various biomasses are 60-88 times higher (14-24kJ/mol on dry basis), while the combustion heat of charcoal is roughly 120 times higher (28-33kJ/g). Accordingly an extreme care is needed with the choice of the initial sample masses when the combustion is studied under controlled experimental conditions, as shown in Section 3.3 Note that the requirements strongly depend on the heating rate, too, as illustrated in Figure 6. The leftmost TGA experiment (green) was measured with a low sample mass (0.35 mg) at a low heating rate (1°C/min). The central experiment (blue) was measured with a similarly low sample mass at a much higher heating rate. The mass loss rate, expressed as –dm/dT (%/°C) has similar magnitudes in the figure. The corresponding –dm/dt values,

however, strongly differ, the peak maximum observed at the fast heating rate (2.14%/s) is ca. 50 times higher than its counterpart at 1°C/min (0.044%/s). This is a general consequence of the kinetic equations at linear heating rates. As a rule of thumb we may assume that the heat flux needed for an endothermic reaction or the heat flux produced by an exothermic reaction is nearly proportional to the heating rate.
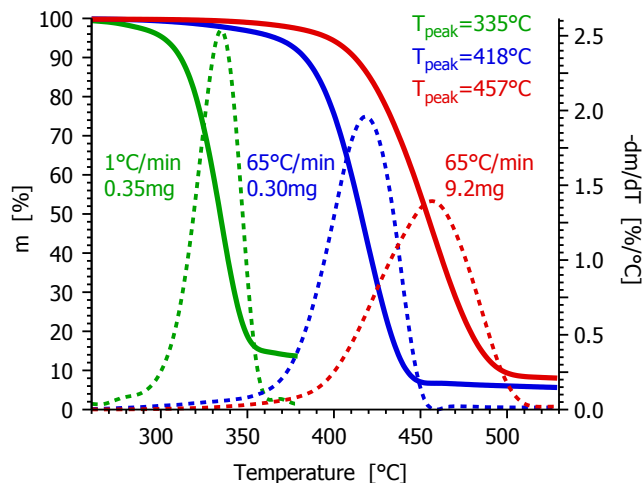

Figure 6. Effect of the heating rate and the sample size on the TGA experiments.[22] Sample: Whatman filter paper CF-11. The temperature, T, is the value measured by the thermocouple of the equipment. Bold solid lines: normalized sample mass (expressed as percent of the initial sample mass and plotted as function of T). Thin dashed lines: mass loss rates expressed as a derivative by the temperature, $–dm/dT$ (%/°C). The initial sample masses and heating rates from left to right were: 0.35 mg and 1°C/min (green); 0.30 mg and 65°C/min (blue); 9.2 mg and 65°C/min (red).

2.4. Biomass Pyrolysis in Sealed Vessels. Around 1990 MJA's attention turned gradually to the charcoals. Surveying the existing biomass results, he concluded that the most valuable pyrolysis product is the char. He carefully collected the available literature information on the methods leading to increased charcoal yields.[25] The most important factor proved to be the fate of the tars because tars can react further in secondary reactions forming more chars and volatiles with lower molecular weight. We studied these processes by DSC (differential scanning calorimetry).[26] The samples were placed into sealed crucibles and heated at a heating rate of 5°C/min. In this way the formed volatiles remained together with the sample, increasing the pressure in the vessels, and reacted further under pressurized conditions. Cellulose, a hemicellulose, woody species and herbaceous species were studied. The overall reaction turned to be exothermal in all cases after heating the samples to the temperatures where the reactions had measurable rates. Particularly marked effects were observed in the cellulose experiments, as shown in Figure 7. When more sample mass was loaded into the same volume, the reaction temperature decreased while the DSC curve became sharper, as shown in Fig. 7a. Similar results were obtained when the available volume was decreases (Fig. 7b). These observations indicate the catalytic effect of the formed

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products. In a third series of experiments the effect of water was examined by studying dried cellulose (curve red), cellulose with the usual moisture content under the Hawaiian climate (magenta curve) and cellulose samples with added water (dark teal and black curves. In this way the marked catalytic effect of the water was proved.[26] (Remark: Figure 7 was constructed from the experimental data that were used in the corresponding kinetic evaluations, one year later.[8] The rest of the experimental data have been lost since 1992.)
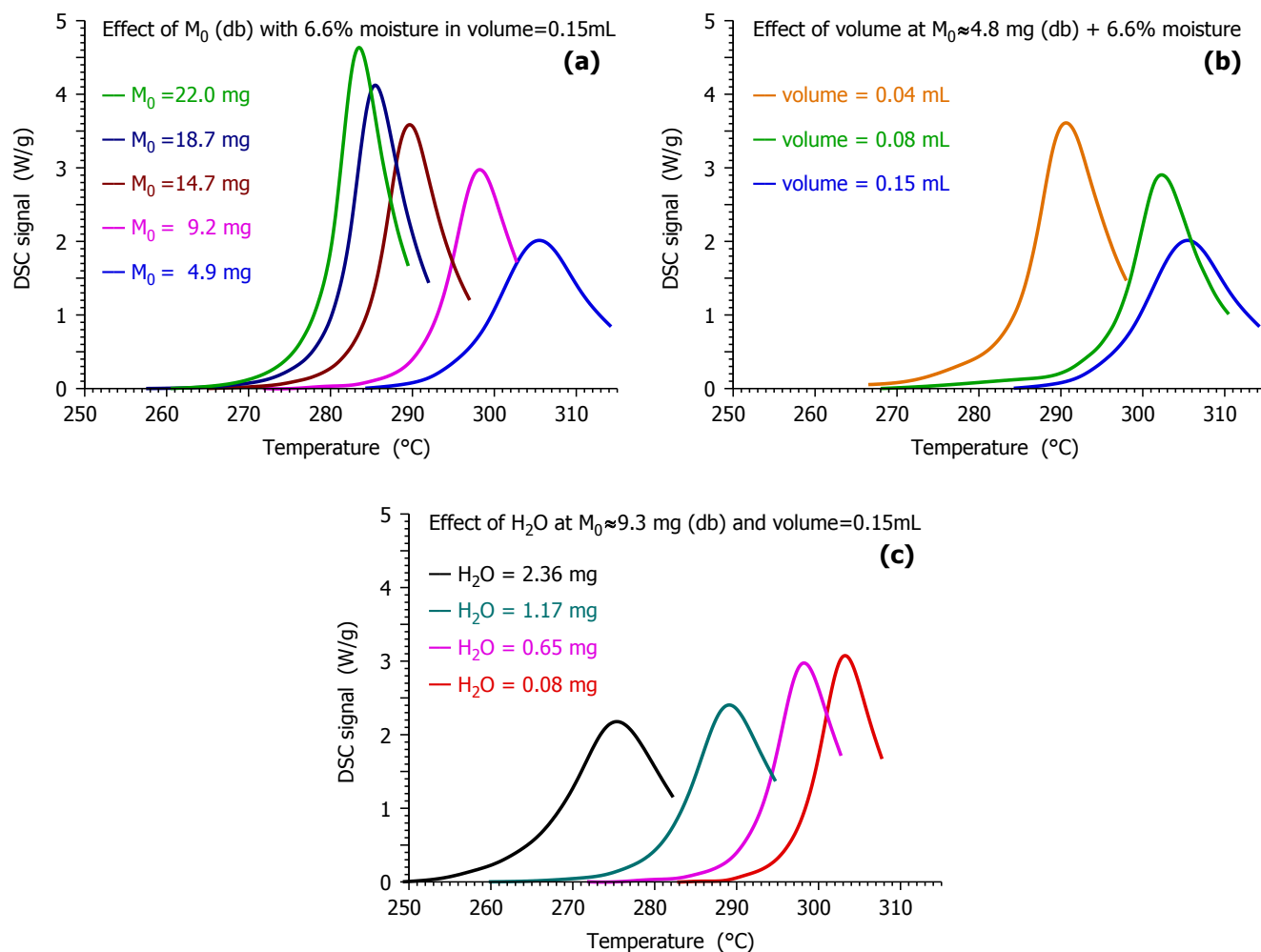

Figure 7. Effect of initial sample mass (a), reaction volume (b), and H_2O content (c) in sealed sample holders measured by DSC at 5°C/min heating rate.[26] M_0 denotes the initial sample mass on a dry basis (db).

In a subsequent work[8] the corresponding kinetics and mechanism were studied. Two competitive reactions were considered: one branch was the regular pyrolysis, and another branch consisted of two consecutive reactions catalyzed by the presence of H_2O. Note that the H_2O in a closed system arises from three sources: the feedstock contained ca. 7% moisture, extra water was added in part of the experiments, and H_2O is an important volatile product of the pyrolysis. The objective function of the optimization was

slightly modified by adding a normalization by the heights of the experiments, h, as mentioned in the Introduction:

$$of = \sum_{k=1}^{N_{exper}} \sum_{i=1}^{N_{points}} \frac{\left[X_k^{obs}(t_i) - X_k^{calc}(t_i)\right]^2}{N_{points} h_k^2} \qquad (2)$$

In this work the number of experiments evaluated simultaneously, N_{exper}, was 9 and 7. (The available 16 experiments were evaluated in two groups for the reasons outlined in the original publication.[8]) Due to the approximate nature of the model, the model parameters were allowed to be slightly different in the different experiments. A good fit was obtained between the experimental and the calculated data. Nine experiments with varying cellulose mass, moisture, and quantity of extra water were described by almost identical parameter sets, proving that the same processes take place under different experimental conditions and that the model gives an acceptable description of these processes. The results indicated that the reaction starts with cellulose hydrolysis, which may be followed immediately by decomposition reactions to give intermediate products. The model provided a rougher approximation at the highest sample loadings where the partial pressure of the product water could reach saturation point. In these cases liquid phase water was also present during the pyrolysis.

3. PROPERTIES AND USAGE OF HIGH YIELD CHARCOALS

3.1. Charcoal Characterization by TGA-MS. Since the mid-nineties MJA and his coworkers developed modern methods to produce high-yield charcoals[27-30] and our cooperation shifted towards the investigation of the charcoals that were produced in Hawaii. The first of this series dealt with the TG, TG-MS and FTIR characterization of high-yield biomass charcoals.[31] Two examples are shown from this work. Figure 8 compares the behavior of charcoal samples taken from the top and bottom parts of the reactor that was used for the charcoal production.[31] A TGA experiment with a stepwise temperature program was used. During the heating, an isothermal section of 30 min at 130°C separated the drying and devolatilization sections. A second isothermal section of 60 min at 380°C was used to study the peculiarities of the low temperature devolatilization. It is interesting to note that the amount of volatile matter capable of devolatilization at this temperature is almost completely exhausted within an hour. Upon further heating, the devolatilization restarted. The sample from the top of the reactor released considerably more volatiles during the 375°C isothermal heating than the sample of the bottom fraction, indicating that the devolatilization was lower in the top of the reactor during the production of the charcoal. However, the two samples showed nearly identical behavior in the last 18 minutes of the isothermal at 375°C and during the subsequent non-isothermal heat-up.
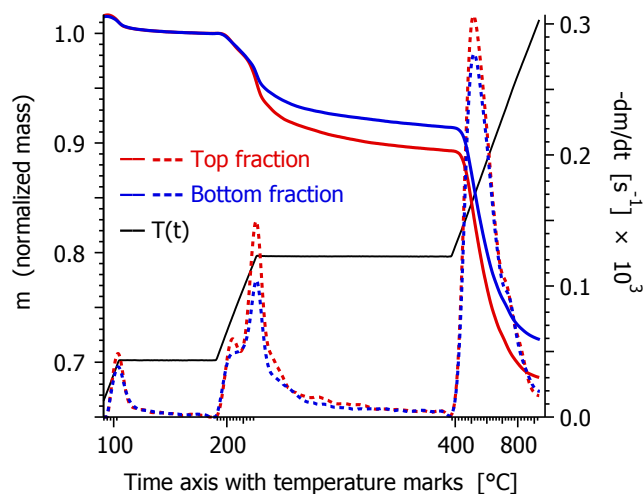
Figure 8. Effect of the feedstock position in the reactor on the properties of the charcoals.[31] Normalized sample mass (solid lines) and mass loss rate curves (dashed lines) are shown as function of time on macadamia nutshell charcoals taken from the top (red) and the bottom (blue) parts of the reactor. The temperature program (thin black line) contained an isothermal of 30 minutes at 133°C, an isothermal of 60 minutes at 375°C and non-isothermal ramp sections with a heating rate of 20°C/min.
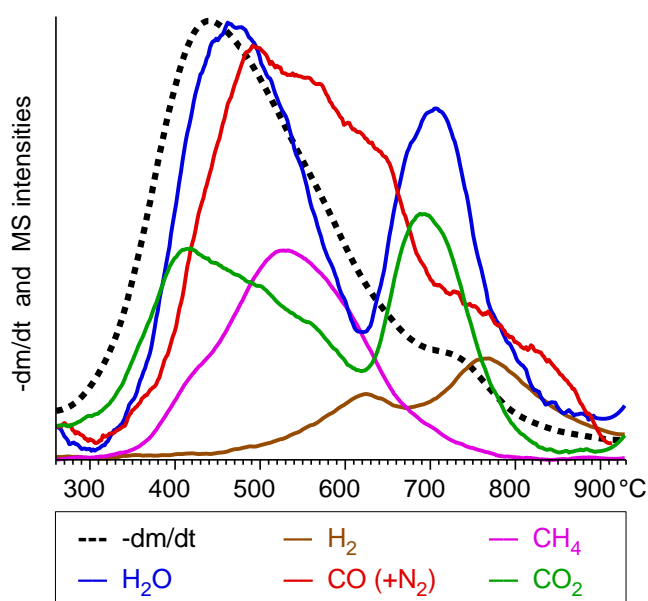

Figure 9. Mass loss rate (black dashed line) and mass spectrometric intensity curves (colored solid lines) during the devolatilization of a macadamia nutshell charcoal sample at a heating rate of 10ºC/min.[31] (The scale factors of the MS intensity curves were chosen proportional to the molecular mass of the corresponding ions, to express better their contribution to –dm/dt.)

Figure 9 shows TGA-MS results on the top fraction char sample. Noteworthy are the double peaks of the water (blue) and CO_2 (green) ion intensity curves, indicating two regions of the devolatilization. Below 600 °C the decomposition of the nonaromatic structures and the splitting off of the aliphatic side groups and functional groups take place. At higher temperatures, the aromatic compounds merge into

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larger units, releasing the excess hydrogen and their oxygen heteroatoms in the form of H_2O, CO, CO_2, and H_2. Methane also formed in both regions, but its intensity decreased to zero around 800 °C.

3.2. Kinetics of Charcoal Devolatilization. Charcoals contain 10-30% volatile matter.[32] A devolatilization by heating in inert environment highly increases the electrical conductivity and opens the ways for further uses of the biocarbons.[33] The construction of fuel cells from biocarbons appeared to be a particularly promising way for biomass utilization that time.[34] Accordingly we studied further the reactions that take place during the heating of the charcoals in inert atmosphere.[35] The charcoals have a rather complex and irregular chemical structure.[36] Accordingly the considerations derived during the many decades of coal research[37] formed the basis of our work. The best available way to represent the complexity of the coals was the use of a distribution activation energy model (DAEM). The large number of different reacting species are mathematically described by an infinite number of parallel reactions in a DAEM. To avoid an infinitely high number of model parameters, the reactivity differences between the species are described by the distribution of one parameter, the activation energy. To keep the number of unknown parameters on a low level, a distribution function, usually a Gaussian is assumed.[37] Based on this concept, we carried out further TGA – MS experiments and studied the kinetics behind the observed results using the state-of-the-art methods available then:[35]

(i) More than one DAEM was assumed because the charcoal devolatilization takes place in very wide temperature domain where different type of reactions occur (as outlined in the previous section);

(ii) The evaluation was based on more than one experiment.

(iii) The series of experiments evaluated together included linear and stepwise *T(t)* programs (as outlined in the Introduction);

(iv) The method of the least squares (eq. 2) was employed;

(v) The DAEMs were solved numerically along the given *T(t)* functions at each set of parameters that arose during the minimization of the least squares sum by the parameters. A high precision numerical method was employed that was freshly published by Donskoi and McElwain[38] when we started this work.

A single DAEM was enough for the observed intensities of CH_3^+, $C_2H_3^+$, and $C_2H_5^+$. Two parallel DAEMs were needed for the double peak of the H_2^+ intensity (which was shown in Figure 9). Four DAEMs were needed for the description of the overall –dm/dt curve. We were unable to obtain a reliable kinetic description for the mass spectrometric intensities associated with the evolution of H_2O, CO, and CO_2 because the corresponding MS intensity curves were distorted by the following complicating factors: (i) these compounds react with each other via reversible reactions on the surfaces of the sample, the equipment walls and the deposited impurities (tars) and (ii) the tar, depositing in the various parts of the equipment during an experiment reacts with the oxygen traces in the system and contributes to the H_2O, CO, and CO_2 evolution at higher temperatures. On the other hand, the model for the CH_3^+ intensity proved to be suitable for prediction tests, too, that proved its reliability. In a test evaluation, the kinetic

evaluation was based only to a fast and a slow linear $T(t)$ experiments and the resulting kinetic parameters gave a good description for the stepwise experiment, too, as shown in Figure 10. Moreover, the model obtained from the top fraction sample could predict the methane evolution from the bottom fraction sample, too (except a scale factor), indicating that the same decomposition processes took place in both samples.
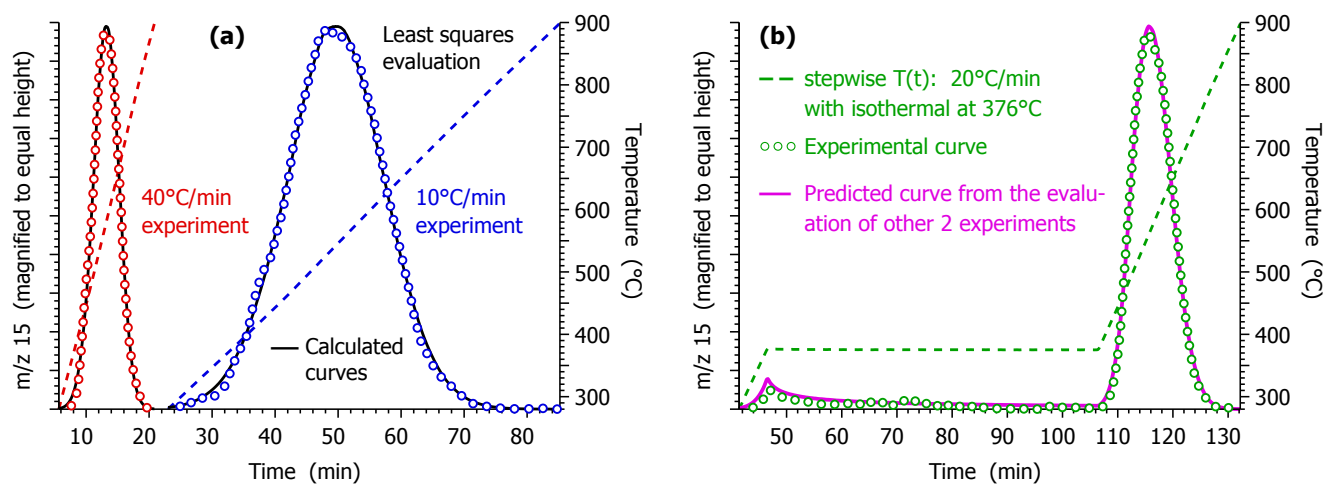

Figure 10. The kinetic parameters obtained from the CH_3^+ intensity curves of two linear $T(t)$ experiments (part **a**) were able to predict the experimental data at a stepwise $T(t)$ (part **b**).[35] Notation: temperature (dashed lines); experimental ion intensity curves (open circles); their best fitting counterparts from the kinetic evaluation (black solid lines); and the curve predicted from other experiments (magenta-colored solid line).

3.3. Kinetics of Charcoal Combustion in the Kinetic Regime. Many different uses are known and can be developed for charcoals. In the cooperation a special way of activation energy production was studied,[39] and the potential use of biocarbons in fuel cells.[34,40] Nevertheless, the most important application is still the combustion. We studied the combustion behavior of charcoals under well-defined conditions, in the kinetic regime, in two works. The first work, published in 2006,[41] dealt with corncob charcoals produced by flash carbonization.[30] Samples from the top, middle and bottom parts of the reactor were investigated. A special charcoal produced from partly demineralized feedstock was also involved in the work. The second study, published this year,[10] dealt with charcoals from Norway spruce and its forest residues. In that work the behavior of the flash carbonization charcoals was compared to charcoals that were produced in a high-pressure TGA under well-defined conditions. Despite the different charcoals and different goals, the two works contained several common elements. Among others, both studies were based on TGA experiments with particularly low sample masses (0.2 – 1 mg). Charcoals have a high reactivity with oxygen, while the reaction heat of their combustion is huge (28-33kJ/g).[32] Accordingly small sample masses and slow heating rates should be chosen to avoid self-

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heating or self-ignition. Otherwise the sample might burn in a split second and the researcher cannot even guess its true temperature. The problem is illustrated in Figure 11. The use of low sample masses requires extreme care in the experiments and careful baseline corrections. Nevertheless, this is the only way to get dependable information on the combustion processes by TGA or other sort of thermal analysis. This looks to be a simple, basic, well proven fact. Nevertheless, most of the present TGA works on charcoal combustion are based on experiments with much higher sample masses (up to 5-10 mg).[10] A possible explanation is the assumption that a part of the TGA apparatuses available nowadays cannot follow the very fast changes. (Because their mechanical inertia is too high and/or their software damping is set inappropriately.) If so, an uncontrolled, fast combustion is not obvious for the researchers.

The charcoals are usually not homogenous; they contain more and less reactive parts. This heterogeneity was approximated by assuming three fractions with different reactivity in both works. Self-accelerating kinetics is frequently observed for char burn-off. This behavior is caused by the opening and growth of the internal pores as the combustion proceeds. There are theoretical models for this effect that were deduced for ideal chars. We can hardly expect their perfect fulfillment for real charcoals that contain grains with irregular geometry; minerals that can catalyze the combustion; and other sources of heterogeneity. Accordingly an empirical model was used that can mimic a wide variety of self-accelerating kinetic behavior.[10,41]

Both works were based on the simultaneous evaluation of experiments with linear and non-linear temperature programs because the information content of the experimental series with linear $T(t)$ is rather limited.[42] Figure 12 shows the curve fitting and the partial curves at two non-linear temperature programs.
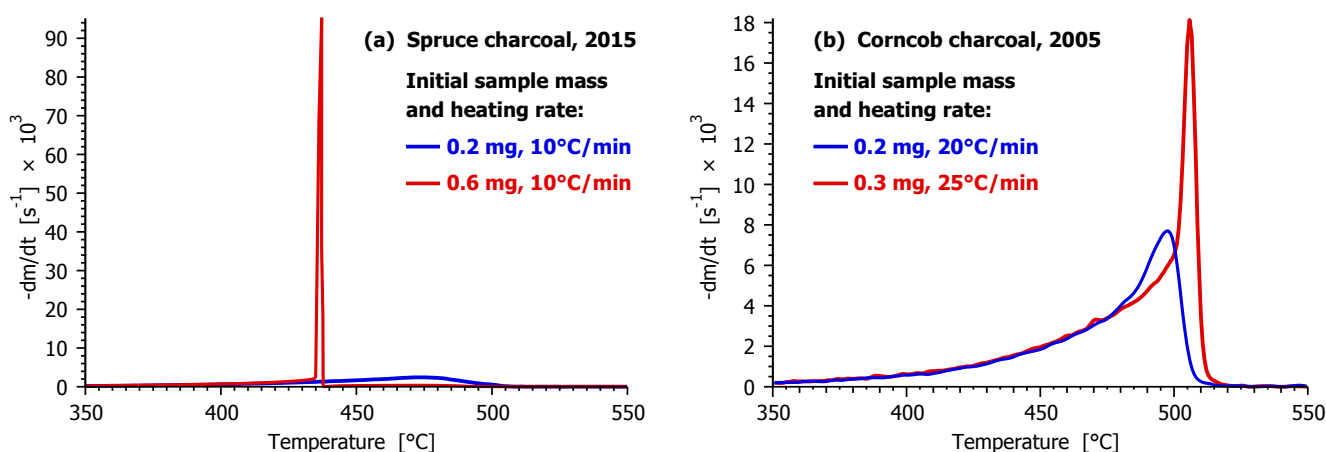

Figure 11. Problems arising from incorrect sample mass – heating rate choice in a recent work[10] (part **a**) and in an earlier work[41] (part **b**). The red-colored mass loss rate curves reflected and uncontrolled self-heating. Note that the charcoals (spruce and corncob), the makers of the equipment (TA Instruments and Perkin Elmer), and the countries of the experiments (Norway and Hungary) differed in the two works.
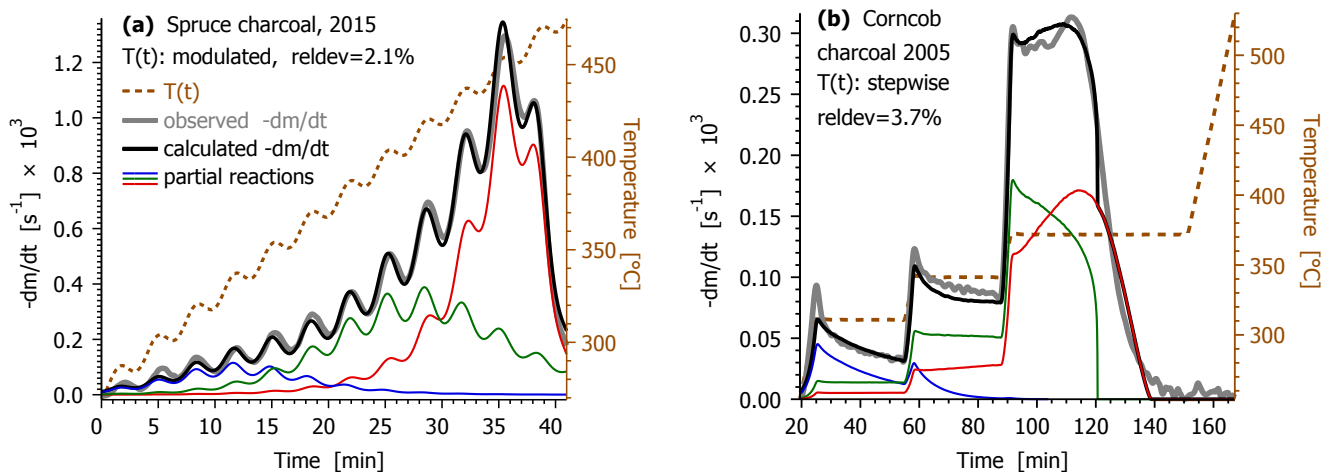
15

Figure 12. Curve fitting and partial curves at a modulated temperature program[10] (part **a**) and at a stepwise temperature program[41] (part **b**). See part **a** for the notations. The term "reldev" in this figure is the root mean square difference between the observed and the calculated curves expressed as percent of the highest observed value.[10,41]

4. CONCLUSIONS

(1) The results of a particularly long scientific cooperation were surveyed from the points of view of the present times.

(2) The work started with pyrolysis studies. The aim was to clarify the factors that lead valuable volatile products ("sirups"). For this purpose the kinetics and mechanism of the biomass pyrolysis was studied with a particular emphasis on the behavior of the cellulose component.

(3) Later the interest of the work gradually shifted to the solid products of the pyrolysis: chars, charcoals and biocarbons. Hence the formation, properties and uses of these products were studied in the second phase of the publication. Here the research topics included the formation of activated carbons by novel ways; the transformation of charcoals to carbons with high electrical conductivity; the use of the biocarbons in fuel cells; and the study of the combustion kinetics under well-defined conditions, in the kinetic regime

(4) Methods and evaluation procedures were established for a dependable kinetic modelling of complex materials and processes. This part of the work had been started before the cooperation by elaborating methods for the simultaneous least squares evaluation of experiments with linear and non-linear temperature programs.[6]

(5) The reliability of the experiments and the experimental conditions necessary for a true kinetic control were also discussed.

(6) The surveyed results were clarified by figures that (i) have not been published earlier (Figures 1, 5, and 11a); (ii) were constructed by the reprocessing of 25-30 year old experiments (Figures 4 and 7); (iii)

or were restyled and upgraded for a better overview. Besides, two photos were also published as a sort of commemoration of Michael J. Antal, Jr.

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