Pyrolysis of pellets made with biomass and glycerol: Kinetic analysis and evolved gas analysis

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Abstract

Glycerol is a co-product compound of biodiesel production with an interesting heating value. In this work pyrolysis kinetic parameters for a pellet made with a mass fraction of 90% sawdust and a mass fraction of 10% glycerol are derived through thermogravimetric analysis. A new parallel reaction scheme with four components (cellulose, hemicellulose, lignin and glycerol) is adopted and the kinetic triplet for each component is derived using a model fitting approach applied to this particular kind of pellet. The isoconversional method Kissinger-Akahira-Sunose is employed both to provide initial values for model fitting simulations and to check final results. Results show that activation energies and pre-exponential factors are respectively: 149.7 kJ mol1 and 1.98*1011 s 1 for hemicellulose, 230.1 kJ mol1 and 1.84*1017 s 1 for cellulose, 154.3 kJ mol1 and 5.14*109 s 1 for lignin, 74.5 kJ mol1 and 2.17*105 s 1 for glycerol with a first reaction order for all components, except for lignin (n ¼ 2.6). Through evolved gas analysis it was demonstrated that the thermal degradation of glycerol contained in the pellet can increase hydrogen content in pyrolysis gases.

1. Introduction

Glycerol is the main co-product of the first generation biodiesel industry with potential energetic applications. It has been demonstrated that [1] using glycerol in a CHP unit could supply the entire electricity consumption of a biodiesel plant and 50% of the heat. Raw glycerol cannot be fed easily into a reactor, such as the rotatory kiln IPRP (Integrated Pyrolysis Regenerated Plant), designed and realized at the University of Perugia, see Refs. [2,3]. This is due to the fact that raw glycerol, obtained from transesterification plants, is fluid. For this reason, a promising alternative is to mix biomass and glycerol. In this way glycerol can act as an additive for biomass, improving its characteristics, and providing a biofuel that can compete with other fossil fuels, such as coal. In literature, there are few works on the co-pyrolysis of glycerol with biomass, but with promising results. In [4] a mixture with a mass fraction of 25% crude glycerol and a mass fraction of 75% olive kernels was pyrolysed at two different temperatures (720 and 520 C) to verify which pyrolysis gas contained more H2. From a comparison of the two experiments, it has been noted that a higher pyrolysis temperature leads to an increase of hydrogen volume fraction in the gas of 11.6%. Another work which described copyrolysis of coal with glycerol in a laboratory scale reactor is the one of [5]. In this work, fast pyrolysis has been conducted with mixtures with a mass fraction of 15 and 20% of glycerol and a mass fraction of 85% and 80% of lignite coal at different temperatures (650, 750 and 850 C). The results show that using a mixture with a mass fraction of 20% of glycerol at 850 C resulted in high hydrogen yield (65.44% in volume fraction, normalized). The slow pyrolysis of crude glycerol with corn straw has been described in Ref. [6]. It has been noted that the blend in proportion [1:1] had a good heating value and produces a gas which is rich in hydrogen. Other works present glycerol combustion with low rank coal and developments in biomass kinetics (see Refs. [7e10]). The authors of this work have

already pyrolysed pure glycerol in the project TERVEG, funded by the Italian Ministry of Agriculture, Food and Forestry with National funding call ''bando bioenergetico DM 246/2007, GU No. 94 del 27/11/2007, see Ref. [7]. In this new work, it is proposed to mix wood pellets with glycerol. This has not been done so far for energy purposes. The idea to produce pellets using glycerol as an additive is original. For this reason, it has been conducted an experimental campaign on glycerol pellets in the framework of the European project BRISK (Biofuels Research Infrastructure for Sharing Knowledge, website: http://briskeu.com/). The experimental campaign was managed by Bioenergy 2020þ (http://www.bioenergy2020.eu/). A first publication on the economic feasibility of the energetic valorisation of glycerol pellet has been already published by the authors in the 23rd European Biomass Conference and Exhibition, see Ref. [11]. The study proposed in this paper aims at the determination of pyrolysis kinetic parameters for pellets made by glycerol and biomass, using TGA analysis. These parameters will permit to simulate the pyrolysis process happening in a rotary kiln working with glycerol pellet, this process can be useful to produce part of the energy required by a biodiesel plant, as shown in Ref. [11]. Being the slow pyrolysis process characterised by low heating rates, to be sure that glycerol actually pyrolyses instead of evaporating during the heating of the pellet, evolved gas analysis was also performed to check pyrolysis gas composition during the whole thermal degradation process. The novelty of the paper is due to the fact that pellet with glycerol as an additive has never been produced nor tested in pyrolysis experiments. Mass loss in biomass pyrolysis is commonly described with a parallel reaction scheme with 3 components (cellulose, hemicellulose and lignin) (see Ref. [12]). In this work, it will be discussed for the first time how to describe the co-pyrolysis of biomass and glycerol. The calculation of kinetic parameters such as activation energies, pre-exponential factors and order of reaction for all the pseudo-components is of fundamental importance to provide data for developing detailed kinetic schemes such the one of Ranzi and the RAC for biomass (see for example [13,14]).

2. Materials and methods

2.1. Materials

Softwood pellets with a diameter of 6 mm were bought at a commercial retailer in Umbria (Italy), and were produced by HS Holzexport Schuster Gesellschaft m.b.H. from species belonging to the fir genus grown in Austria, Innsbruck. Pure glycerol was bought at a chemicals retailer in Umbria, Italy. Different pellets produced from glycerol were tested at the Biomass Research Centre laboratories and durability was measured with a New Holmen TekPro machine. Preliminary tests have shown that pellet obtained by mixing glycerol with sawdust in a mass ratio higher than 15% has a durability which is not satisfactory at the moment. For this reason, it has been decided to produce pellets with a mass fraction of glycerol of 10% and a mass fraction of sawdust of 90% and to perform pyrolysis tests in a reactor and in a thermogravimetric balance. It has to be taken into consideration that [15] tested similar concentration of glycerol to produce pelletized pig feed and they report that the durability of the pellets could increase by 9% just by adding glycerol, so the effect of this additive is also dependent on the nature of the material with which it is mixed. The mixture of wood pellets with pure glycerol was prepared in a 1 L volume glass jar mixing 500 g of wood pellets and 55 g of glycerol (see Fig. 1). At first, the material was mixed for 20 min, then, when no drops of glycerol were visible inside the jar, the raw material was put in a plastic bag. After two or three days the wood pellets had completely absorbed glycerol, which decreased pellets bulk density from 640 kg/m3 to 485 kg/m3 . The results of material characterization are shown in Table 1. It should be noticed that the HHV of wood pellets (19.2 MJ/kg db) and pellets with pure glycerol (19.0 MJ/kg db) are similar. Pure glycerol HHV is about 18.6 MJ/kg. Pellets with pure glycerol have a lower ash content and higher volatile content. Wood pellets have a higher fixed carbon content.

2.2. Instrumentation

Pellets durability was measured using a New Holmen TekPro machine, according to the standard [16]. LECO TGA 701 was employed for proximate analysis, LECO Truspec CHN was employed for ultimate analysis and LECO AC-350 was employed for calorimetry. Analysis were performed both at the Biomass Research Centre (Perugia, Italy) and at the laboratories of Bioenergy 2020þ (Graz, Austria).

Fig. 1. Raw material used, A-pure glycerol, B- wood pellets, C- glycerol-wood pellets.

The procedures used for material characterization and the standards were already proposed in Ref. [17]. For the TG kinetic analysis, a Netzsch STA 409 CD was used (available at the laboratories of the University of Graz and Bioenergy 2020þ). For sample preparation, a milling machine was used to produce a powder of the average dimension of 0.2 mm, to be used in the thermogravimetric analysis (TGA). Six tests were performed using samples of 20 mg, taken from a mass of 100 g of pellets containing a mass fraction of 10% glycerol. Three heating rates were used: 5-10-20 K min1 with two repetitions. Tests were repeated also with pellets without glycerol. Milled samples of pellets were introduced in the ceramic crucible. The sample and the ceramic crucible were then inserted in the thermogravimetric balance and heated under a nitrogen atmosphere. The first step was heating the sample to a temperature of 110 C, with a heating rate of 20 K min1 , and the sample was maintained at this temperature for 15 min. After completing the evaporation step, the sample was heated at 900 C with different heating rates (5-10-20 K min1). This procedure was applied for all the samples. A baseline was also made after each test to subtract the common noise of the machine to the signal obtained by each test. In the thermogravimetric diagrams, the range of temperatures between 110 C and 500 C was selected because this is the region where the main devolatilization process and formation of char occurs. Evolved gas analysis was performed in a batch reactor, already presented in Ref. [18]. The reactor is realized in silicon carbide because this material does not react with the tested biomass. The sample holder (see Fig. 2) contains 3 to 5 thermocouples placed at different heights in the biomass bed and it is inserted in the reactor which is preheated by electrical furnaces and flushed with nitrogen. Flue gas samples are extracted from the gas volume above the fuel bed, they are partly treated through dilution and temperature stabilization. Then they are analyzed with two EGA (Evolved Gas Analysis) systems, which outputs are cross-checked to understand the reliability of the measures. The 2 systems used in the tests performed in this work are: Fourier Transform Infrared spectroscopy (FTIR)

(Ansyco) for CO_2, H_2O, CO, CH_4, NO, NH_3, HCN, NO_2, N_2O, basic hydrocarbons and Emerson NGA 2000 using paramagnetism for O_2 and Nondispersive Infrared analysis (NDIR) for CO_2 and CO; heat conductivity for H_2. Pictures of the system are reported in Fig. 3. Two pyrolysis tests, repeated two times, were performed: one using pellets containing 10% glycerol and one using pure pellets, to compare results and evaluate the influence of glycerol on gas composition. The experimental campaign is proposed in Table 2. The temperature of the reactor was set to 500 C. During the tests mass loss has been measured and also pyrolysis gas composition, through FTIR and NDIR systems. The heating ramp in the reactor was about 16 K min1 and so the experiment was comparable with the heating rate of TGA tests. The first experiment (Pyr-SW-1) was performed only to know which was the furnace temperature set-point required to reach inside the reactor 500 C (no nitrogen was flushed). It was noticed experimentally that setting the furnace to a temperature of 650 C a value of 500 C was easily reached inside the reactor. Data acquisition was stopped after maintaining the final temperature for 20 min. Obviously the mass of char obtained from pure pellets is higher than that obtained from pellets with 10% glycerol. For PyrSW-3-Gly and Pyr-SW-4 the following yields were measured: 23% and 26%, respectively. In the first experiment char yield (29.7%) was higher due to the absence of sweeping gas flow; this increased the retention time of the volatiles in the bed, enhancing secondary charring reactions.

Table 1
Material characterization.

Mass fractions of components	Pure glycerol	Wood pellets	Pellets with 10% mass fraction of pure glycerol
Moisture	0%	7.5%	7.1%
Volatiles db	100%	79.04%	89.10%
Ash db	0%	0.41%	0.36%
Fixed Carbon db	0%	20.55%	10.54%
C db	39%	50.01%	49.32%
H db	9%	6.21%	6.44%
N db	0%	<0.1%	<0.1%

Fig. 2. Sample holder extracted after the tests.

Char yield obtained with pellets with glycerol is lower compared to that of pure pellets because of the higer content of volatiles, due to glycerol presence.

3. Theory and calculations

3.1. Kinetics of parallel reaction schemes with pseudo-components

The theory on isoconversional methods is reported in the supplementary material. If an isoconversional method implies different activation energies and pre-exponential factors for each mass loss fraction, another approach can be based on the identification of the decomposition kinetics, not for biomass as a whole, but for its main pseudo-components, that is cellulose, hemicellulose and lignin (see Ref. [12]). Cellulose is a polymer of glucose units, which thermal degradation happens typically in the range of temperatures comprised between 315 C and 390 C (according to [19]). Hemicellulose pyrolysis starts at 220 C and reaches its maximum at 260 C. Lignin is a phenolic compound with high molecular weight. Due to its complex structure, lignin decomposes over a very broad range of temperatures (from 160 to 190 C, when lignin softening happens to 370e400 C, when the cleavage of C-C linkages happens, see Ref. [12]). The reaction of the above mentioned components can be modelled with equation (1) for each ith pseudo-component; also glycerol is considered.

$$\frac{d\alpha_i}{dt} = A_i \exp\left(-\frac{E_i}{RT}\right)(1-\alpha_i)^{n_i} \tag{1}$$

Previous works (see Refs. [20e23]) have shown that the first order model gives a very good approximation for cellulose and hemicellulose. However, for lignin, it was shown (see Ref. [12]) that other reaction models, such as the third order reaction model, can give a better result. The reaction rate of each pseudo-component ($d\alpha_i/dt$) reported in equation (4) can be calculated once that the three kinetic parameters (kinetic triplet) are known: the preexponential factor (A_i), the activation energy (E_i) and the order of reaction (n_i). In a parallel reaction scheme, together with the above mentioned kinetic triplet (A, E and n), another parameter has to be considered: the contribution of each pseudo-component to the overall weight loss. So the kinetics of each pseudo-component is described by 4 parameters (A, E, n and c_i) and the total mass loss can be given by the sum of the mass losses of the single pseudocomponents, see equation (2).

$$\frac{d\alpha}{dt} = \sum_{i=1}^{n} c_i \frac{d\alpha_i}{dt} \tag{2}$$

where c_i represents the contribution of the degradation of the ith pseudo-component to the overall weight loss. A mathematical approach to find the kinetic parameters of each component in model-fitting methods is the nonlinear last squares fitting method. In this method, the objective function is defined as the difference between the experimental and simulated data (3).

$$objective\ function = \sum_{i=1}^{N}\left(\left(\frac{d\alpha_i}{dt}\right)_{exp} - \left(\frac{d\alpha_i}{dt}\right)_{sim}\right)^2 \tag{3}$$

A minimization of the sum of calculated objective functions for Fig. 3. Pyrolysis reactor and Evolved Gas Analysis Systems. Table 2 Batch reactor experimental campaign parameters. Parameters Sample codes Pyr-SW-1 Pyr-SW-2 Pyr-SW-3-Gly Pyr-SW-4 Pyr-SW-5-Gly Final Temperature (C) 500 500 500 500 500 Initial weight (g) 279.1 282.6 263.2 282.1 214.8 Test duration 30 min 30 min 30 min 30 min 30 min Final weight (g) 83.0 76.25 59.75 73.0 49.66 N2 flow (l/min) / 4 l/min 4.5 l/min 4.2 l/min 4.5 l/min Furnace temperature (C) 650-620 C 650-620 C 650-620 C 650-620 C 650-620 C 14 P. Bartocci et al. / Biomass and Bioenergy 97

(2017) 11e19 each heating rate and each corresponding experimental curve (N), will result in the best fitting set of kinetic parameters (3).

Table 2
Batch reactor experimental campaign parameters.

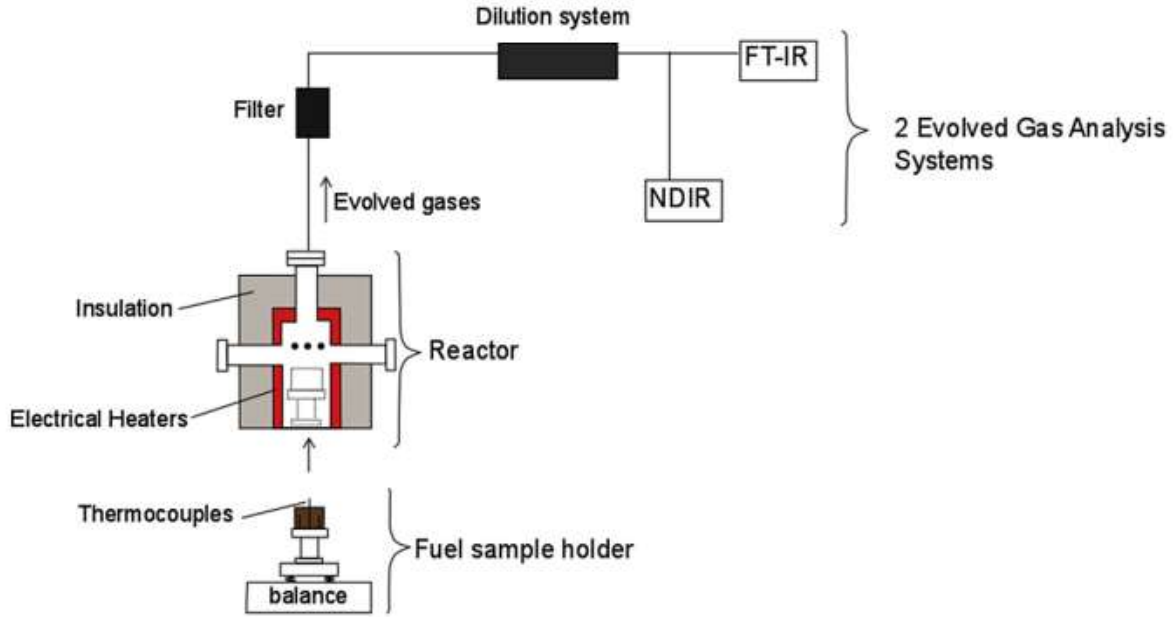| Parameters	Sample codes				
	Pyr-SW-1	Pyr-SW-2	Pyr-SW-3-Gly	Pyr-SW-4	Pyr-SW-5-Gly
Final Temperature (°C)	500	500	500	500	500
Initial weight (g)	279.1	282.6	263.2	282.1	214.8
Test duration	30 min	30 min	30 min	30 min	30 min
Final weight (g)	83.0	76.25	59.75	73.0	49.66
N₂ flow (l/min)	/	4 l/min	4.5 l/min	4.2 l/min	4.5 l/min
Furnace temperature (°C)	650-620 °C	650-620 °C	650-620 °C	650-620 °C	650-620 °C

Fig. 3. Pyrolysis reactor and Evolved Gas Analysis Systems.

To obtain the kinetic constant parameters, the nlinfit routine in Matlab, based on the Levenberg-Marquardt algorithm was used. Being the total mass fixed, the mass of the fourth component can be calculated from the masses of the first three. The minimization is performed for a set of 4*N-1 kinetic parameters if nth order reaction models are employed for all the components, where N is the number of components. Obviously, for the pellet with glycerol, the components will be 4 instead of three: glycerol, cellulose, hemicellulose and lignin. The fit quality can be calculated with equation (4), where S represents the mean squared difference between the calculated and the experimental values and hmax is the maximum value of the DTG curve.

$$fit(\%) = 100 \frac{\sqrt{S}}{h_{max}} \tag{4}$$

3.2. Use of isoconversional methods to control model fitting results

As reported in Ref. [23] and also in Ref. [24], model free approaches can be used to supplement model fitting. In particular, isoconversional method can be used to identify different reactions occurring during thermal degradation and, therefore, to provide useful information to improve and develop model fitting methods based on parallel reactions of the pseudo-components. The basis for this improvement is the chart showing the trends of activation energy (E) against conversion (a), as also reported in Ref. [25]. In this

paper at first, isoconversional activation energy and preexponential factors are calculated and then the obtained information will be used as initial parameters in the fitting process and as a comparison for final results. For the above mentioned reasons isoconversional models can be useful to give confidence that the kinetic parameters obtained and the employed reaction model (e.g. first or nth reaction order) are reliable representations of the actual chemical process taking place.

4. Results

4.1. Thermal decomposition

TG and DTG diagrams of the pyrolysis for the samples of wood pellets with a mass fraction of 10% of pure glycerol at different heating rates (5, 10, 20 K min1) under nitrogen atmosphere are presented in the supplementary material. Fig. 4 shows the comparison between the DTG curve of pure sawdust and sawdust with a mass fraction of 10% glycerol. With the presence of glycerol, a further peak in the range of 200Ce300 C is present, which is due to glycerol volatilization.
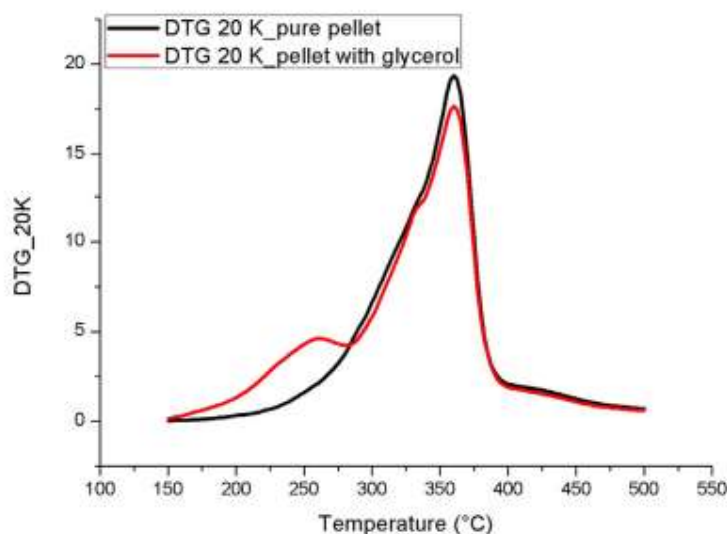

Fig. 4. Comparison between DTG curves of pellet made with pure sawdust and pellet with 10% mass fraction of glycerol at 20 K min^{-1}.

4.2. Isoconversional methods

TGA tests were performed at three different heating rates. Based on what reported [26] and [27] about a comparison among isoconversional methods, the Kissinger-Akahira-Sunose method was employed. The activation energy is calculated for a constant value of conversion (a). The kinetic parameters were calculated from the slope and the intercept of the plot shown in the supplementary material both for glycerol-wood pellets and for pure wood pellets. The graphs with the plots of ln(b/T2 max) versus 1/T are reported in the supplementary material, together with a table showing the correlation factors of the lines. Fig. 5 reports the trends of the isoconversional activation energies versus conversion extent. In Fig. 5 activation energies can be grouped into four reactions. The first group of activation energies is at lower conversion rate and can be attributed to glycerol. The second group is attributable to hemicellulose, the third to cellulose and the fourth to lignin. These assumptions can be checked reporting some arrows in the plot, indicating the conversion extent corresponding to the peak temperature of each pseudo-component when simulated through the fitting approach (see also table A1 of the supplementary material). The points range from 0.02 to 0.84 of conversion with a step of 0.02. A sudden increase of activation energy at

conversion values higher than 0.84 (not shown in the figure) can be ascribed to the fact that values at very high alpha have low correlation coefficient, being the reaction rate very slow and therefore with a high uncertainty. The data reported in Fig. 5 allow to forecast the following values of activation energies: 224 kJ mol1 for cellulose, 154 kJ mol1 for hemicellulose and 64 kJ mol1 for glycerol; these can be used as initial values in the model-fitting method (least squares fitting in a parallel reaction scheme), described below. Concerning lignin behaviour, as it is very difficult to find a peak for this material in Fig. 5, an average value was supposed (191 kJ mol1), comprised in the range of lignin activation energies reported in Refs.[12] and [23]. 4.3. Model-fitting method To describe accurately the pyrolysis kinetics of each component (hemicellulose, lignin, cellulose and glycerol), the parallel reaction scheme with four pseudo-components was used. Figs. 6e8 show the application of the deconvolution method expressed by the objective function proposed in equation (3), which has been implemented for all the heating rates: 5 K min1 , 10 K min1 , 20 K min1 . The kinetic parameters obtained through fitting of experimental data with a parallel reaction scheme with four pseudo-components (cellulose, hemicellulose, lignin and glycerol) are shown in Table 3. Hemicellulose has an activation energy of 149.7 kJ mol1 and a preexponential factor equal to $1.98*10^{11}$ s 1 . Cellulose has an activation energy of 230.1 kJ mol1 and a pre-exponential factor equal to $1.84*10^{17}$ s 1 . Lignin has an activation energy of 154.3 kJ mol1 and a pre-exponential factor of $5.14*10^9$ s 1 . Glycerol has an activation energy of 74.5 kJ mol1 and a pre-exponential factor of $2.17*10^5$ s 1 . The values obtained for cellulose are in accordance to the ones presented by Ref. [28] and the values obtained for glycerol with the ones of [29]; while the values reported for hemicellulose and lignin are comparable with those reported by Ref. [23]. A first order reaction model has been employed for hemicellulose, cellulose and glycerol and a nth order reaction model for lignin. The obtained reaction order for lignin is 2.6, in concordance to what has been exposed in section 3.2. Data are obtained fitting all the three DTGs diagrams with different heating rates (5 K min1 , 10 K min1 and 20 K min1), so that the activation energies that have been found are valid for all the different heating rates, avoiding possible compensation effects. In Table 3 the temperatures corresponding to the decomposition start are also reported, together with the peak and the decomposition end, as obtained by the multi-peak fitting method. Obviously, these temperatures depend on the heating rate, so the average of the three heating rates is reported and also the standard deviation. It can be seen that for glycerol (for example) the standard deviation of the decomposition start is equal to zero because the peak of glycerol obviously starts at the beginning of the thermogram (i.e. at 150 C). The same is for lignin, its peak starts at the beginning of the thermogram and finishes at the end (i.e. respectively 150 c and 500 C). The fit quality is high because it is equal to 1.06% for the heating rate of 5 K min1 , 0.93% for the heating rate of 10 K min1 and 0.92% for the heating rate of 20 K min1 , showing that the employed approach is accurate.
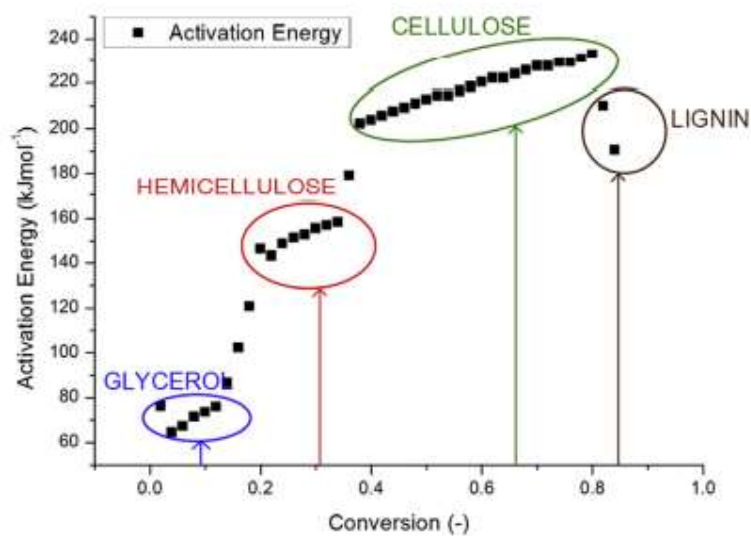
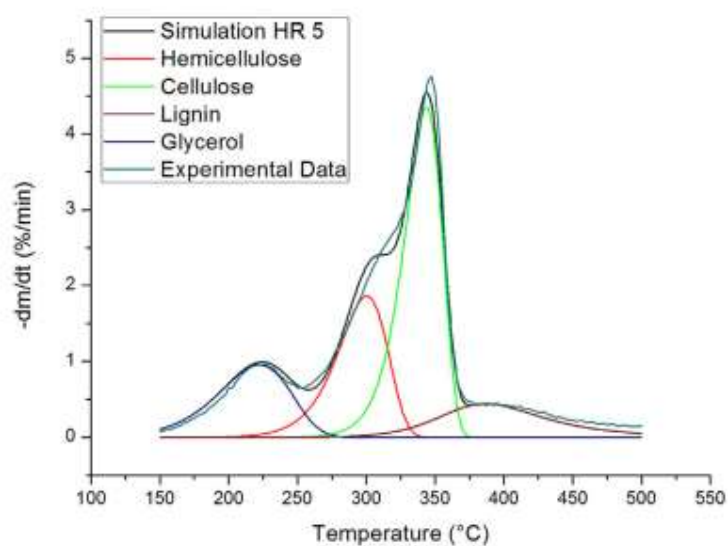**Fig. 5.** Activation Energy as a function of conversion extent.

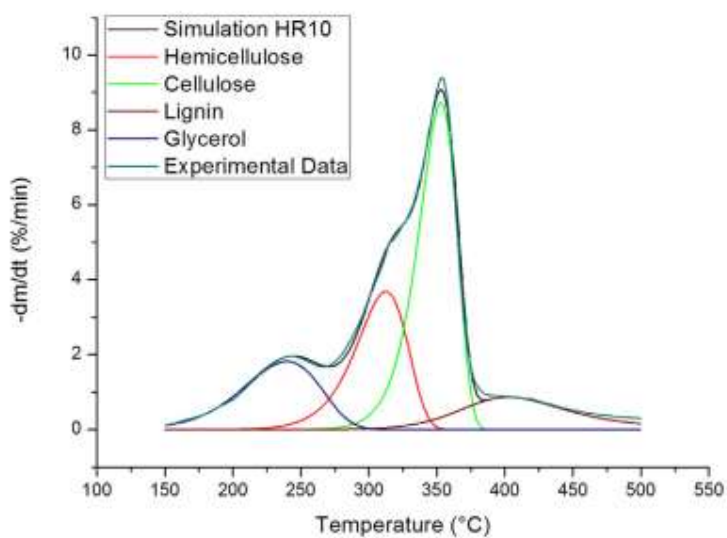**Fig. 6.** Model-fitting method for DTG curves, obtained at 5 K min^{-1}.

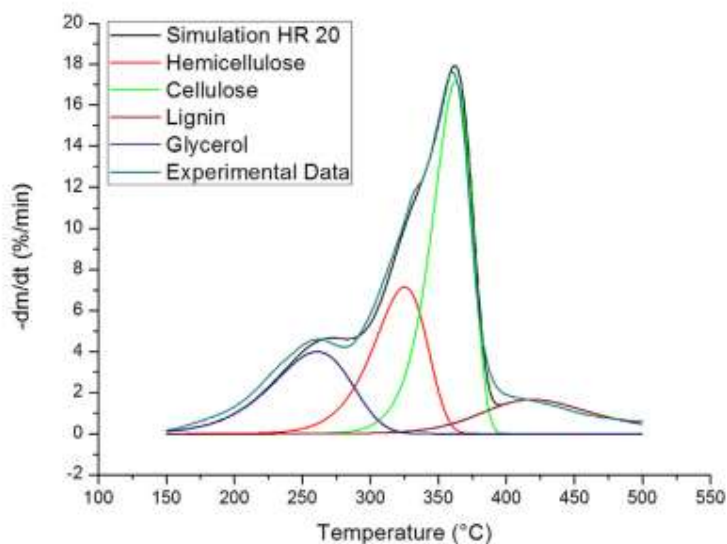**Fig. 7.** Model-fitting method for DTG curves, obtained at 10 K min^{-1}.

Fig. 8. Model-fitting method for DTG curves, obtained at 20 K min^{-1}.

4.4. Validation of results

Isoconversional (model-free) methods can be used also to verify that the data obtained through model fitting are correct. Knowing the value of temperature corresponding to the peaks of the four pseudo-components under study (see Table 3), the activation energy can be calculated at each conversion in the KAS diagram (see Fig. 9).

Table 3
Kinetic parameters from model-fitting method.

Component	Decomposition start	Peak temperature	Decomposition end	E	A	Reaction order
	(°C)	(°C)	(°C)	(kJ mol^{-1})	(s^{-1})	(–)
Hemicellulose	223 ± 9	313 ± 12	352 ± 14	149.7	1.98*10^{11}	1.0
Cellulose	283 ± 7	353 ± 9	382 ± 10	230.1	1.84*10^{17}	1.0
Lignin	282 ± 11	403 ± 16	500 ± 0	154.3	5.14*10^{9}	2.6
Glycerol	150 ± 0	241 ± 19	303 ± 23	74.5	2.17*10^{5}	1.0

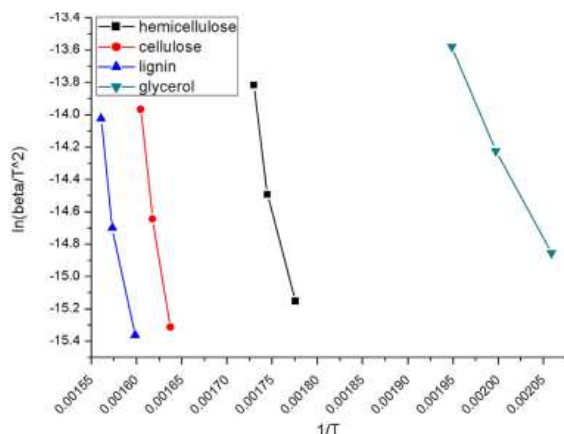**Fig. 9.** KAS method applied to single pseudo-components.

Fig. 9 shows the KAS lines obtained by plotting ln(b/T2) versus 1/ T for the peak temperatures of the four pseudo-components. From Table 3 it can be seen that pure glycerol has maximum decomposition peak at about 241 ± 19 C. The maximum peak for hemicellulose is at about 313 ± 12 C. The cellulose maximum peak is at 353 ± 9 C. Lignin maximum peak is at about 403 ± 16 C. The activation energy was obtained from the slope of the plot shown in Fig. 9. The correlation coefficient was high for all pseudocomponents. The value of R2 for glycerol, hemicellulose, cellulose, and lignin was respectively 0.9946, 0.9588, 0.9847 and 0.9594. Results are promising, the methodology should be repeated with more heating rates available and for more matrices. Table 4 reports the activation energies of the four pseudocomponents, obtained through a model-fitting approach and then applying an isoconversional method (KAS method), at the conversion extent at which each pseudo-component peaks. It can be seen that the parallel reaction scheme with nonlinear least squares fitting method gives similar results, compared to KAS method. Moreover, these values are in the range of literature values.

Table 4
Comparison of activation energies derived from different methods.

Component	Model-fitting	Model-free (KAS)		Literature, see Refs. [23,29,30]
	Activation energy (kJ mol^{-1})	Conversion (α)	Activation energy (kJ mol^{-1})	Activation energy (kJ mol^{-1})
Hemicellulose	149.7	0.29	154.1	80–230
Cellulose	230.1	0.64	224.7	195–286
Lignin	154.3	0.84	190.5	18–200
Glycerol	74.5	0.08	63.7	44–68

It has been shown that mass loss during pyrolysis of a mixture of biomass and glycerol can be described as an extension of the parallel reaction scheme for biomass in order to include glycerol decomposition at low temperatures. Furthermore, the glycerol component is interested by a first order reaction. Further analysis using FTIR, GC-MS or other evolved gas analysis methods (see Ref. [31]) can be used to complement the results provided by TG analysis.

4.5. EGA analysis

To analyze the behaviour of glycerol mixed with sawdust in the pellets evolved gas analysis was performed. The aim was to compare gas composition of pyrolysis products obtained from conventional pellets with that of pyrolysis products obtained from pellets containing glycerol. If glycerol was not actually evaporating but was pyrolysing, forming combustible gases such as hydrogen and methane, the yields of those gases would be higher compared to those of conventional pellets (made with a mass fraction of 100% of saw dust). Fig. 10 shows a comparison of CO, CH4, H2 and HCHO yields obtained from the pyrolysis of conventional pellets and pellets with glycerol. The abbreviation 10%GL corresponds to the average values measured during the experiments: Pyr-SW-3-Gly and Pyr-SW-5- Gly reported in Table 2; while the abbreviation 100%SD represents the average values measured during the experiments: PyrSW-2 and Pyr-SW-4 reported in Table 2. It can be seen that the release of hydrogen in the case of the pellets with glycerol is higher compared to that of the pellet with a weight ratio of 100% saw dust. The same is true for formaldehyde release, which is a typical compound obtained from the degradation of glycerol, as it can be seen from Ref. [32]. On the other hand the release of CH4 and CO show a similar evolution with and without glycerol. What it can be inferred by Fig. 10 is that glycerol once absorbed in the biomass matrix is heated and begins its degradation inside the matrix. In fact glycerol pyrolysis happens mainly through dehydration reactions [32].
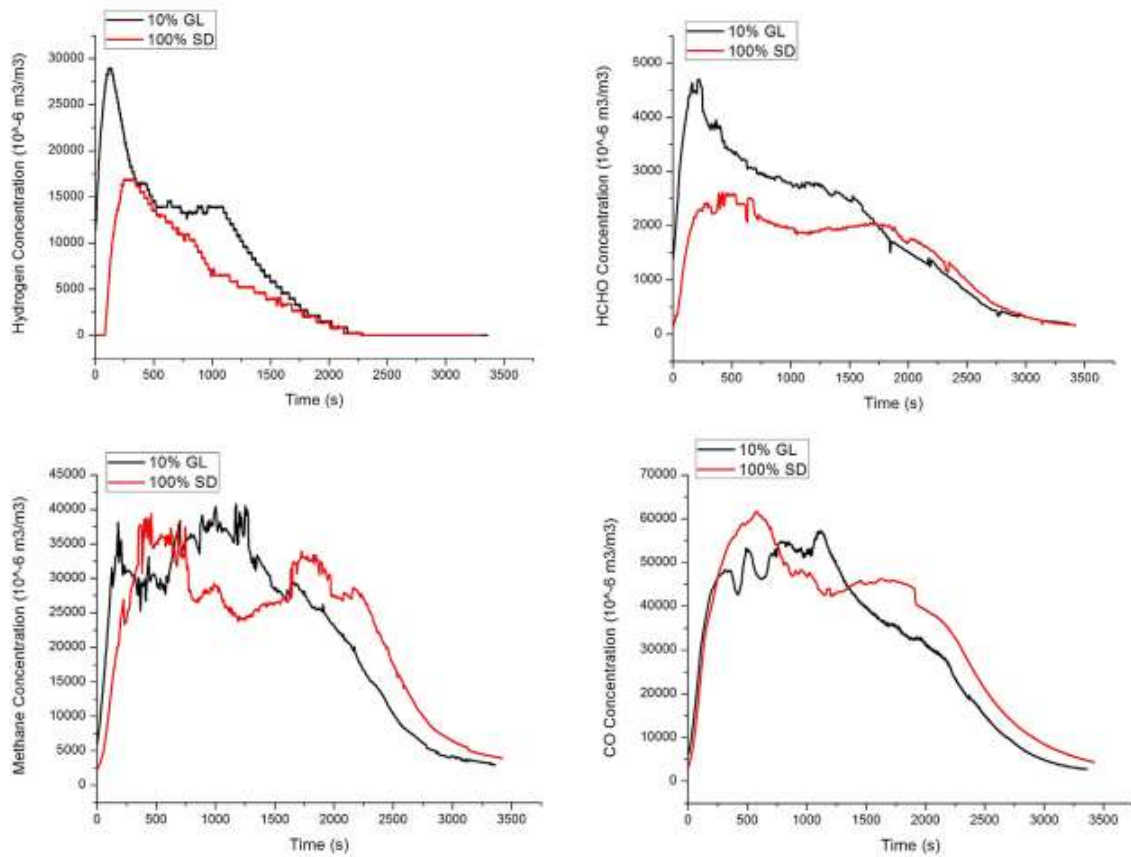

Fig. 10. Evolved Gas Analysis (EGA) results.

5. Conclusions

About 10 kg of pellets containing 10% glycerol and 90% sawdust were prepared at the University of Perugia (Italy) and brought to Bioenergy 2020+ (Austria) to perform TGA kinetic studies. It has been shown that mass loss during pyrolysis of a mixture of biomass and glycerol can be described as an extension of the parallel reaction scheme for biomass, and it can include glycerol decomposition at low temperatures. The

glycerol component decomposition can be described using a first order reaction. The obtained activation energies and pre-exponential factors for hemicellulose, cellulose, lignin, and glycerol are respectively: 149.7 kJ mol1 , 230.1 kJ mol1 , 154.3 kJ mol1 , 74.5 kJ mol1 and 1.98*1011 s 1 , 1.84*1017 s 1 , 5.14*109 s 1 , 2.17*105 s 1 . Evolved gas analysis was performed in a fixed bed laboratory reactor equipped with NDIR and FTIR systems. Through EGA it was demonstrated that the thermal degradation of glycerol contained in the pellets during pyrolysis can increase hydrogen content in pyrolysis gases. It was also demonstrated that glycerol actually reacts and undergoes pyrolysis (instead of evaporation), as confirmed by the early release of H2 and HCHO.

Acknowledgements

Appendix A.

Theory about Isoconversional methods

The thermal decomposition of biomass measured by the thermogravimetric analysis can be visualized by plotting the mass loss (TG) curve against the temperature (or time), or differential mass loss (DTG) curve, also referred to as mass loss rate, against temperature. For biomass fuels this shows a very characteristic thermal decomposition mechanism, which can be described by Arrhenius equation, as expressed in equation 1.

$$\frac{d\alpha_i}{dt} = A_i exp\left(-\frac{E_i}{RT}\right)(1 - \alpha_i)^n \qquad (1)$$

Where α_i is the mass loss fraction and it is give by equation (2).

$$\alpha_i = \frac{m_{0,i} - m_{t,i}}{m_{0,i} - m_{f,i}} \qquad (2)$$

and (1-α)n is the nth order reaction model. As reported in [1], isoconversional methods have the advantage to eliminate the reaction model from the kinetic computations (this is the reason why isoconversional methods are also named as "model-free"). This can be made based on the principle that the process rate at constant conversion extent is only a function of temperature.

The Kissinger-Akahira-Sunose (KAS) method is isoconversional. In the KAS method, the activation energy is calculated for a given value of mass loss fraction (α), where the heating rate is expressed as β. The activation energy can be calculated from the slope of the line obtained by plotting ln(β/T2max) vs 1/T. Pre-exponential factor can be calculated based on the intercept of the same graph.

$$ln\left(\frac{\beta}{T^2{}_{max}}\right) = \ ln\left(\frac{AR}{E}\right) - \frac{E}{R}\frac{1}{T}$$ (3)

Supplementary graphs and tables

Figure A1 and A2 show the trends of TG and DTG performed at three heating rates (5K/min, 10 K/min and 20 K/min). The data shown in figure A1 and A2 represent the basic data used in the calculations reported in the manuscript.
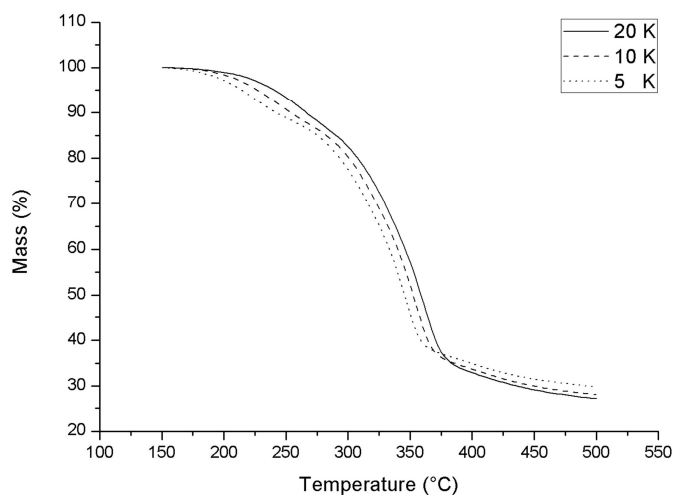

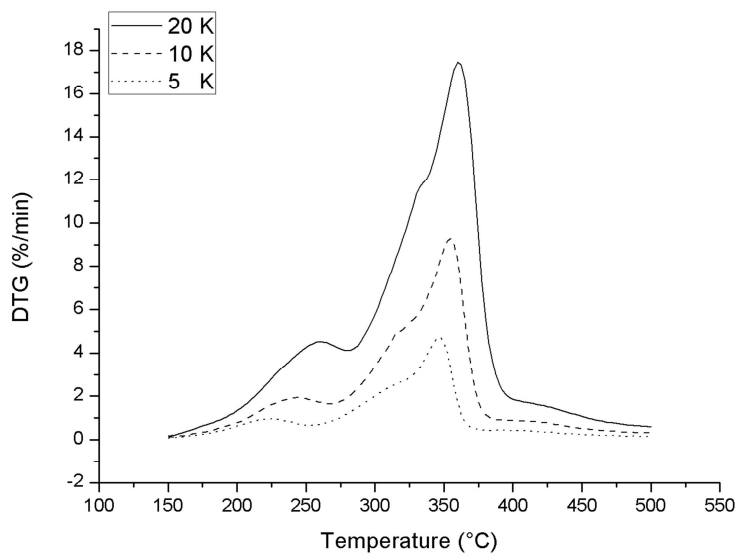Figure A1: TG diagrams for pellet with 10%w glycerol

Figure A2: DTG diagrams for pellet with 10%w glycerol

In the TG diagram from temperature 110°C to about 200°C a small mass change can be observed. With the increase of temperature also the mass loss increases rapidly. Above 370°C the mass changes slowly, until

the temperature of 500°C is reached and mass loss approaches to zero. The solid residues were about 30% of the initial weight for all analysed samples.

The temperatures in which the peaks of the multi-component model are found, are reported in the graph of alpha (defined in equation (2) of the manuscript) to find which α (conversion extent) corresponds to the peak temperature (see figure A3).
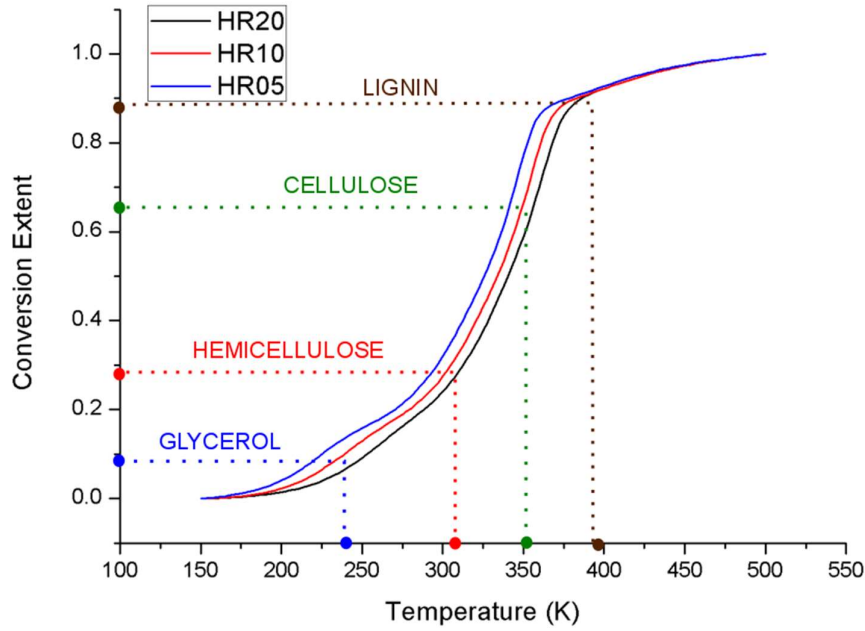

Figure A3: Conversion extent in function of temperature

The average conversion extents, depending on peak temperature, are reported in table A1.

Table A.1: Average conversion extents corresponding to pseudo-component peak temperature in the fitting model

Pseudo-component	Peak Temperature (°C)	Conversion Extent
Hemicellulose	313±12	0.29
Cellulose	353±9	0.64
Lignin	403±16	0.84
Glycerol	241±19	0.08

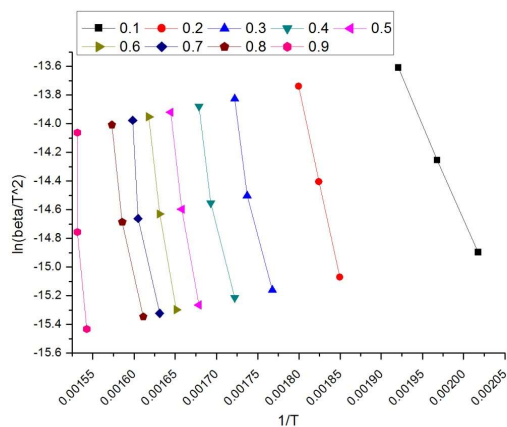Figure A4 shows Kissinger-Akahira-Sunose method results.

Figure A4: Kissinger-Akahira-Sunose method

For the study the range of conversion from 0.02 to 0.84 was taken into consideration. As it can be seen in Table A2, dealing with the pyrolysis of glycerol-wood pellets, the apparent activation energy at low conversion gradually increases, reaching values above 230.0 kJ/mol and then decreases at high conversions. The calculated correlation coefficient is high for all the conversion levels up to 0.8 (with one exception at 0.36) and then decreases. This is due to the difficulty of defining the exact mass corresponding to the end of reaction (mf) and that the reaction rate is very slow and therefore with a high uncertainty. For this reason the activation energies of conversions above 0.84 are not reported.

Table A2: Activation energy from KAS method for glycerol-wood pellets

Conversion (α)	Ea (kJ/mol)	R^2 (-)
0.02	76	0.973
0.04	64	0.981
0.06	67	0.981
0.08	71	1.000
0.1	74	1.000
0.12	76	1.000
0.14	87	0.993
0.16	102	1.000
0.18	121	0.991
0.2	146	1.000
0.22	143	0.959
0.24	149	0.959
0.26	151	0.959
0.28	153	0.959
0.3	155	0.959
0.32	157	0.959
0.34	158	0.959
0.36	179	0.884
0.38	202	0.985
0.4	204	0.985
0.42	206	0.985
0.44	207	0.985
0.46	209	0.985

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[1] Vyazovkin, S., kinetics of stimulated Isoconversional Thermally Processes, pp. 1-239, ISBN 9, DOI: 319-14175-6

0.48	211	0.985
0.5	213	0.985
0.52	215	0.985
0.54	215	0.985
0.56	216	0.985
0.58	218	0.985
0.6	220	0.985
0.62	222	0.985
0.64	222	0.985
0.66	224	0.985
0.68	226	0.985
0.7	227	0.985
0.72	227	0.985
0.74	229	0.985
0.76	229	0.985
0.78	231	0.985
0.8	233	0.985
0.82	210	0.884
0.84	191	0.959

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