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THERMAL ANALYSES OF DIFFERENCES FOR WOODY SPECIES DEPENDING ON SOIL CONDITIONS*

Mykola Kharytonov[1], Viktoriia Kalyna[1], Nadiia Martynova[2], Margaryta Sbytna[3]**

[1]Dnipro State Agrarian and Economic University, Dnipro, Ukraine,
[2] Oles Honchar Dnipro National University, Dnipro, Ukraine
[3]Institute of Energy Crops and Sugar Beet of NAASU, Kyiv, Ukraine

Abstract

Specific characteristics of soil substrates and different climatic conditions indirectly affect the thermal behavior of wood mass. Differences in the wood thermal characteristics of the different trees grown under different soil conditions most likely depend on changes in the composition of the extracted substances, which are most susceptible to environmental influences. The substrata properties affect the thermal characteristics of the wood. Changes are manifested in the speed of reactions, the content of volatile components and changes in the ash content of wood. In turn, extractive substances contribute to reducing or increasing the proportion of carbon in wood, changing the rate of mass loss, shifting the temperature intervals of thermal degradation.

Keywords: fast-growing energy trees, soil conditions, wood thermal features,

1. Introduction

Wood biomass is an important renewable energy resource with a short carbon cycle (Poletto et al., 2012). This circumstance has led to an increased interest in the wood thermal characteristics including the kinetic laws its thermal degradation (Adeleke et al., 2019). The chemical composition of hardwood varies widely. This is due to a number of factors. The most important of them are the species accessory, soil and climate conditions. The chemical composition plays a decisive role in determining the quality of wood as an energy source. The quantity and ratio of the wood components determine its thermal features and the

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** Corresponding author: email: kharytonov.m.m@dsau.dp.ua

specificity of decomposition in the combustion process (González Martínez et al., 2018). Thermal degradation of wood can be represented by the sum of reactions of thermal destruction of the main components as hemicellulose, cellulose and lignin. Thermal decomposition of hemicellulose, cellulose and lignin occurs in the intervals of 225-325, 305-375 and 250-500°C, respectively (Shen et al., 2009). Cellulose is characterized by greater thermal stability than hemicellulose and lignin (Vichnevsky et al., 2003). Extractive substances of wood contribute to main components thermal destruction. Despite the small amount, they can significantly affect both the physical and thermal characteristics of wood. Extractive substances, in turn, are most susceptible to environmental factors (Sebio-Puñal et al., 2012), (Rodrigues et al., 2017). One of the tasks of renewable energy is to obtain high-quality products in short-rotation coppice with fast-growing woody species. One solution to this problem is to expand the list of these species, including promising clones of willow, poplar and paulownia (Ates et al., 2008; Grønli et al., 2002; Kharytonov et al., 2017; López et al., 2012; Rosúa and Pasadas, 2012). Currently, improving the efficiency of the use of woody biomass focuses mainly on research and improvement of combustion technologies (Lyytimäki, 2019). There is an opinion that the energy properties of woody biomass depend on the soil, climate and type of wood. According to the influence of the type of wood, some studies have been conducted and published (Khalil et al., 2008; Liu et al., 2012; Prins et al., 2006), while the influence of the conditions for growing raw materials on the characteristics of wood has not been studied completely.

The main objective of the research was to study the thermal characteristics of new for renewable energy wood fast-growing species (*Elaeagnus*, *Ailanthus*, *Paulownia*), and their comparison with traditional willow (*Salix*) and poplar (*Populus*) grown in short-rotation coppice. The second task was to test the hypothesis about the influence of wood age, climatic conditions and soil types on the thermal behavior of wood during its combustion.

2. Materials and methods

The research was carried out at Pokrov land reclamation station of Dnipro State Agrarian and Economic University, standing at 47°39'N, 34°08'E, with an elevation of 60 m. The station is located in the Dnipropetrovsk region at the Nikopol manganese ore deposit. This is the steppe zone of Ukraine with moderately continental climate: dry and hot summer and moderate winter. The hottest month is July with the average temperature +22.0°C, the coldest is January with the average temperature -4.1°C. The region is characterized by an unstable rainfall with often prolonged droughts in the summer. The annual rainfall is 465 mm, 274 mm of which belongs to the warm period (April-October) and 191 mm refers to the cold period (November-March). Samples of spontaneous flora of new for renewable energy wood fast-growing species (*Salix×hybrida*, *Populus×hybrida*, *Elaeagnus angustifolia and Ailanthus altissima*) were taken from plants of 3 years age, grown on black soil (BS), gray-green clay (GGC) and a mixture of loess-like loam (LLL) and red-brown clay (RBC) also passed through a period of long-term phytomelioration. During last decade Paulownia tree is using in agroforestry because of its fast growth rate and the high amount of the wood quantity generated in a short time period. Each Paulownia tree aged 5 –7 years old can generate 1 m^3 timber in a surface with density of 2000 plants/ha, offering a total production of 330 t/ha. In the areas planted with a smaller number of plants per surface unit can reach a production of 150 t/ha (Icka et al., 2016). Paulownia clone in vitro 112 saplings were obtained from “Paulownia Group Ukraine”and planted in May 2017 on black soil and loess-like loam (LLL) that has passed the period of long-term phytomelioration. The humus content in rock substrata did not exceed 1.5 %. The ratio of humic and fulvic acids was in the range 0.2-0.5, which indicates a low level of humus accumulation and active destruction of the soil mineral part.

To compare wood biomass thermal indexes after growing under different climate and soil conditions one clone of hybrid poplar named Ghoy was selected. Clone cuttings were taken from trees grown on technosol presented as mixture of loess-like loam and red-brown clay, and from trees grown on sod-podzolic soil at the Boyarka scientific station under forest-steppe zone conditions. This zone is characterized by a temperate continental climate with mild winters and warm summers. The average annual temperature is +8.4ºC. The warmest month is July with the average temperature +20.5°C, the coldest is January (-3.5ºC). The average annual precipitation is 600-620 mm. The agrotechnical conditions for growing the studied plants were the same in all variants of the experiment. The thermal characterisctics of energy trees wood were measured using thermogravimetric analysis. A physical experiment on thermal destruction of samples using TGA was chosen as the research method. Thanks to this, it became possible to obtain quantitative estimates of the composition of various energy components of wood biomass samples. It was performed at derivatograph Q-1500D of the "F.Paulik-J. Paulik-L. Erdey" system. The weight of sample used for analysis was 100 mg. The differential mass loss and heating effects were recorded, and the results of the measurements were processed using software package supplied with the device. The samples of biomass were analyzed dynamically at a heating rate of 10°C/min in an air atmosphere. The reference substance was aluminum oxide. As a criterion for assessing the thermal stability of biomass, the activation energy of thermal oxidative destruction was determined using the double logarithm method of Broido. In addition, during the experiments, a qualitative analysis of the wood samples combustion process was performed. Data received in experiments accomplished were processed by statistical methods using the software package StatGraphics Plus at significance level of 0.95%.

3. Resutls and discussion

The thermal decomposition of studied wood plants takes place in two periods: the decomposition of volatile compounds and the destruction of the main components: hemicellulose, cellulose and lignin (Table 1).

The first period occurs in temperature range 50-180ºC and characterized by low speeds and percentage of weight loss. The second period, in turn, is divided into two or three stages. Three stages are clearly traced on the DTG curves in the process of thermolysis of *Elaeagnus* wood: decomposition of hemicellulose with an extreme point of 270ºC, destruction of cellulose with a peak in the temperature range of 290-300ºC, and decomposition of lignin without pronounced peaks (Fig.1). The greatest mass loss is observed during the second stage and was 53.4-54.4%.

Table 1. Thermal decomposition of wood

Elaeagnus								
Stage	LLL+RBC				GGC			
	Interval, ºC	Extremum point, ºC	Maximum rate, %/min	Weight loss,%	Interval, ºC	Extremum point, ºC	Maximum rate, %/min	Weight loss,%
I	50-170	90	11.2	8.0	30-180	90	17.8	15.0
II	170-280	270	32.8	24.6	180-280	270	27.6	21.6
III	280-360	290	32.8	28.8	280-360	300	37.4	32.8
IV	360-540	400	10.2	33.32	360-490	380	7.2	23.0

Share of residual mass 5.28 %	Share of residual mass 7.6 %

Populus								
Stage	BS				GGC			
	Interval, °C	Extremum point, °C	Maximum rate, %/min	Weight loss,%	Interval, °C	Extremum point, °C	Maximum rate, %/min	Weight loss,%
I	50-160	90	10.6	7.8	60-160	90	9.4	5.8
II, III	160-400	300	33.0	60.6	160-390	300	42.0	61.2
IV	400-550	440	8.4	8.2	390-550	440	11.4	7.2
Share of residual mass 7.8 %					Share of residual mass 7.2 %			
Salix					***Ailanthus***			
Stage	LLL+RBC				LLL+RBC			
	Interval, °C	Extremum point, °C	Maximum rate, %/min	Weight loss,%	Interval, °C	Extremum point, °C	Maximum rate, %/min	Weight loss,%
I	60-190	90	10.8	8.4	50-180	100	7.6	5.05
II, III	190-390	300	39.4	59.4	180-420	320	38.4	64.64
IV	390-540	450	10.8	23.2	400-590	460	9.2	24.6
Share of residual mass 9.0 %					Share of residual mass 5.67 %			

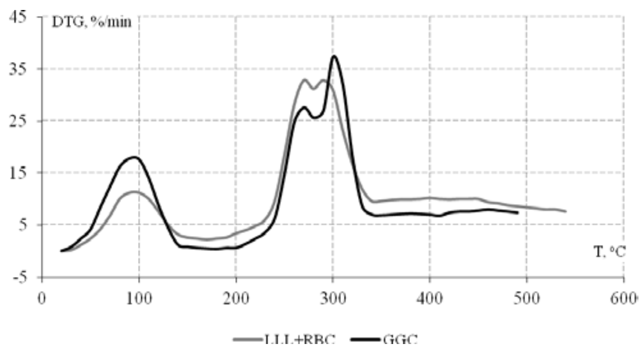


Fig.1. DTG curves of thermal decomposition of *Elaeagnus* wood

The type of the thermolysis of *Salix* and *Populus* is almost the same. The wood of these species has a similar amount and composition of hemicelluloses. The temperature ranges of decomposition of hemicellulose and cellulose overlap in both species. It is manifested by the presence of only one peak on the DTG curves at a temperature of 300°C (Fig.2). The weight loss at this stage was 59.4-61.2%.The decomposition of lignin and the formation of a non-combustible residue take place in the temperature range 390-550°C with a weak peak at 440-450°C.

For *Populus, Salix* and *Elaeagnus,* the decomposition stages of cellulose and lignin are accompanied by a pronounced exothermic thermal effect (Fig.3).

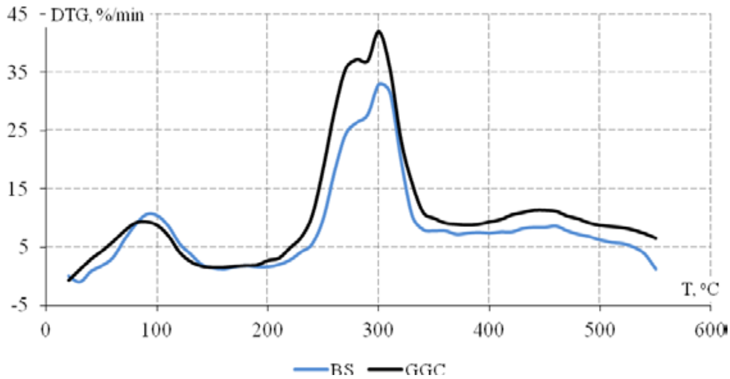


Fig.2. DTG curves of thermal decomposition of *Populus* wood

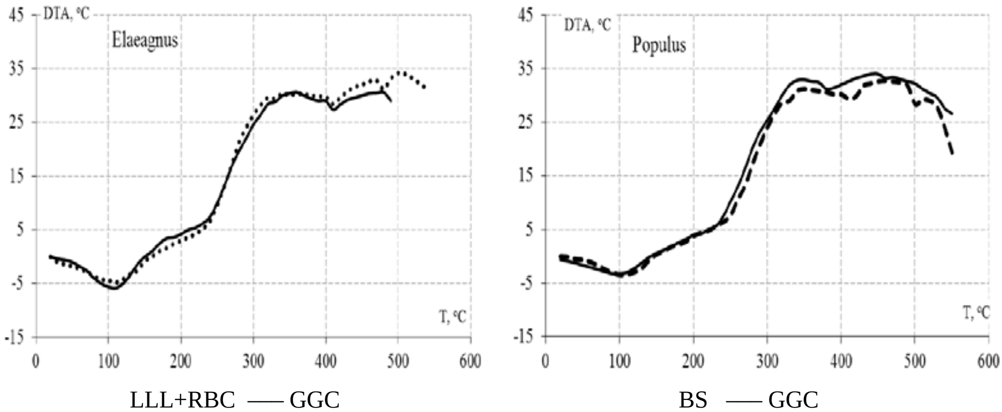


Fig.3. Thermal effects of wood thermolysis on the example of Elaeagnus and Populus

Differences in thermal characteristics of plants growing on different substrates are observed. Thus, the thermolysis in wood of *Elaeagnus* plants growing on gray-green clay begins and ends at lower temperatures than in wood on a technical mixture (LLL+RBC). The rate of destruction at the initial stage is 59.0% more, weight loss is 87.5%. At the stage of decomposition of the main components, hemicellulose and lignin decompose at a lower rate, and cellulose, on the contrary, with a higher. The share of residual mass is greater: 7.6% versus 5.3% on LLL+RBC.

Populus wood has noticeable differences in the rate of decomposition of holocellulose. It was 27.3% more than that grown on black soil comparative with wood grown on gray-green clay. The combustion of raw materials was more complete on this substrate as well.

Thermolysis of *Ailanthus* wood begins at 50-60°C and ends at 590-610°C. In the first period, the process speed is low, and weight loss doesn’t exceed 7%. The extremum point was observed only at a temperature of 320°C in the decomposition range of holocellulose (Fig.4).

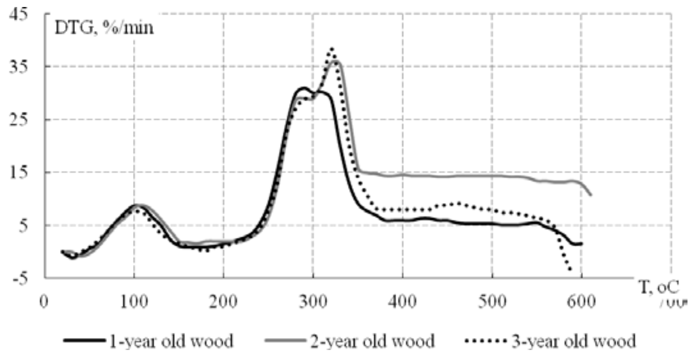


Fig.4. DTG curves of thermal decomposition of Ailanthus altissima wood

Depending on the age of the wood, weight loss was 56.0-64.6%. The holocellulose content and its decomposition rate are highest in three-year-old wood. Higher decomposition rates of lignin and its highest content are characteristic of two-year old wood. At the initial stage of thermolysis, the highest activation energy is characteristic for 1-year old wood (63.32 kJ/mol), and at the stage of decomposition of the main components, for 3-year old wood (66.87 kJ/mol). The data of thermogravimetric analysis revealed some differences in the process of wood combustion of Paulownia clone 112 grown on different substrates (Table 2).

The process of decomposition of wood components began at a temperature of 60-70°C. The first stage of water evaporation and removal of volatile compounds in the sample grown on loess like loam was longer, the process speed was 32% higher. However, the percentage of mass loss was almost the same in both versions of the experiment. This can be explained by the higher thermal stability of wood grown on loess like loam. The LLL wood mass sample initial activation energy was bigger on 34 kJ/mol comparative to 50.6 kJ/mol of BS sample or up to 67%. The LLL woody sample initial stage was characterized also by endothermic reactions with the most pronounced thermal effect in the temperature range of 110-120 °C (Fig.5).

The stage of decomposition of holocellulose is characterized by exothermic reactions and consists of two phases – destruction of hemicellulose and decomposition of cellulose. Due to the relatively large number of hemicelluloses and their specific composition, the beginning of decomposition of hemicellulose is delayed, and the extreme point is shifted to the zone of higher temperatures. Therefore, the destruction ranges and extremum points of hemicellulose and cellulose partially overlap. This is shown by only one peak on the DTH curve in this region (Fig.6).

Table 2. The wood thermal decomposition of Paulownia clone 112 grown it two substrata

Stage	***LLL***				***BS***			
	Range, °C	Extrem. point, °C	Max. rate, % /min	Weight loss,%	Range, °C	Extrem. point, °C	Max. rate, %/min	Weight loss,%
Water evaporation	60–190	110	7.4	5.4	70–160	110	5.6	4.82
Holocellulose degradation	190–400	270	46.2	67.6	160–350	270	41.8	58.09
Lignin destruction	400–500	410	6.6	14.4	350–500	360	6.4	24.52
Burnout of coke residue	500–560	–	4.2	7.0	500-560	–	2.2	6.64

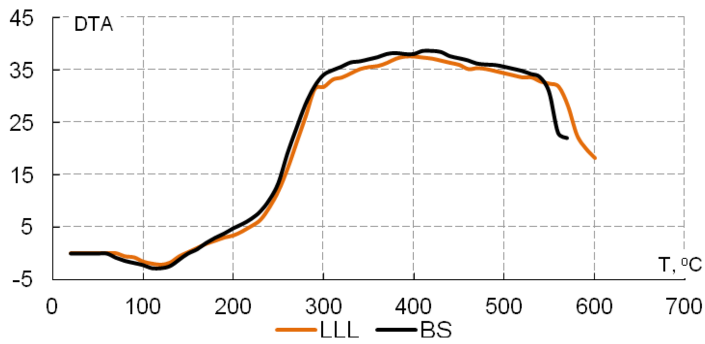


Fig.5. DTA curves of Paulownia clone 112 wood thermolysis

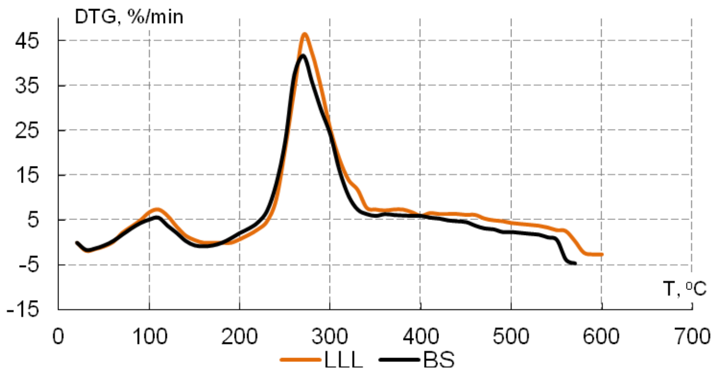


Fig.6. DTG curves of Paulownia clone 112 wood thermolysis

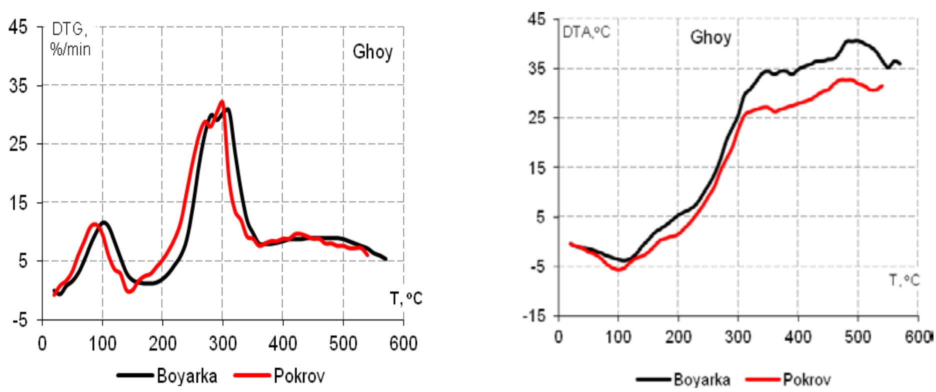
The stage of holocellulose decomposition in a wood sample of *Paulownia* grown on loess-like loam ends later. The maximum decay rate and mass loss were 10% higher. The activation energy values in both variants did not differ significantly from each other and were 65.1 kJ/mol (LLL) and 63.8 kJ/mol (BS). The most pronounced thermal effect was observed in the zone of cellulose destruction. The main decomposition of lignin, which began at the previous stage, occurs in the temperature range of 350-500°C and is accompanied by the greatest thermal effects. The process is quite slow, with no pronounced peaks. However, one extreme point was observed at temperatures of 410°C (LLL) and 360°C (BS). Thus, the main decomposition of lignin in wood grown on black soil occurred at lower temperatures. The mass loss in this sample was also greater. The combustion of coal formed at the previous stages and the formation of a non-combustible residue occurred at the last stage at a temperature of 560°C. This process was faster in the loess-like loam variant. The percentage of residual mass was 5.6% (LLL) and 5.9% (BS). Comparative thermogravimetric analysis of “Ghoy” poplar clone grown follow the same scheme of planting in Boyarka and Pokrov stations is shown Table 3 and fig 7. Destruction processes begin at temperature 30-40°C. The initial stage of evaporation of water and volatile compounds takes place against the background of endothermic reactions with weakly expressed thermal effects in the temperature range of 90-120°C.

Table 3. Thermal characteritics of Populus woods decomposition. Clone "Ghoy"

Stage	***Boyarka***				***Pokrov***			
	Interval, ºC	Extremum point, ºC	Max. rate, %/ min	Weight loss,%	Interval, ºC	Extremum point, ºC	Max. rate, %/ min	Weight loss,%
I	40–180	100	11.6	8.2	30–150	90	11.2	9.2
II	180–290	280	30.0	21.8	150–280	270	28.8	24.8
III	290–380	310	30.8	31.2	280–370	300	32.0	29.6
IV	380–570	440	9.0	31.6	370–540	420	9.6	26.2
Share of residual mass 7.2%					Share of residual mass 10.2%			

The speed of the process is low. One peak at a temperature of 80-90ºC was observed in this range. The weight loss of was 8-9%. This stage in the wood of trees grown at the Pokrov reclamation station was shorter, and the process passed at lower temperatures. The stage of decomposition of holocellulose in the "Ghoy" clone is divided into two phases: destruction of hemicellulose and cellulose. Therefore, two peaks are observed on the DTG curves in this region (Fig.7a): one peak at a temperature of 270-280ºC (decomposition of hemicellulose) and a second peak at a temperature of 300-310ºC (decomposition of cellulose). In wood from Pokrov, the mass loss during decomposition of hemicellulose is slightly higher than in wood from Boyarka.

The lignin decomposition process occurred at approximately the same rate in both variants of the experiment. However, in the Boyarka case, the extremum point was shifted to the region of higher temperatures, and the percentage of mass loss was greater. At the stages of cellulose and lignin degradation, the most pronounced exothermic effect was observed, and in the wood from the Boyarka, it was higher (Fig.7b). Moreover, in this variant, the combustion of wood was more complete –share of residual mass was 7.2% versus 10.2% in the Pokrov case.



a b

Fig.7. DTG and DTA curves of "Ghoy" poplar clone wood thermal destruction in Boyarka and Pokrov stations

4. Conclusions

A preliminary analysis of the influence of species belonging, soil, climate conditions and wood age on the thermal characteristics of wood biomass was carried out. The decomposition ranges of hemicellulose and cellulose in the “Ghoy” *Populus* clone and *Elaeagnus* wood are separated. This made it possible to observe two peaks in the DTG curves in the region of destruction of holocellulose. In the range of holocellulose destruction, *Salix*, *Populus*, *Ailanthus* and *Paulownia* clone 112 wood has only one peak, because of the large amount and specific composition of hemicellulose. The beginning of the decay is shifted to higher temperatures and the extreme point is overlapped by the peak of cellulose decomposition. Thermolysis of all studied species is accompanied by endothermic reactions in the first period of destruction (evaporation of volatile compounds) and exothermic in the second (degradation of the main components). Stages of cellulose and lignin decomposition are characterized by pronounced exothermic thermal effects. The thermal indexes of wood slightly change with age. So, in the 3-year old wood of *Ailanthus*, the content of holocellulose is greater, and the lignin is less than in the 1-year old and 2-year-old. The main differences in the wood thermal characteristics of *Paulownia* and *Populus* clones grown on different substrates are changes in the duration of thermolysis stages, shifts in temperature intervals and extreme points, changes in mass loss rates. This phenomenon is most likely due to the influence of substrates on the complex of extractive substances of wood, which largely determine its thermal behavior. To identify more accurate patterns it is necessary to conduct a more detailed systematic analysis of what is planned in the near future.

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