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ROLE OF THERMODYNAMIC PROCESSES IN PLANT LEAF GAS EXCHANGE SYSTEM FOR ASSIMILATION OF CO_2 EMISSIONS FROM THE AMBIENT AIR

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Highlights

- When temperature in the leaf gas exchange system changes, the thermodynamic parameters describing the condition of moist air also change.
- When plant leaf temperature in the leaf ventilation system changes, the aggregate water vapor state changes in the internal leaf surface, and the state of water vapor changes in cavities.
- The formation and change of nano water films on the internal surfaces of plant cavities, create conditions for chemical processes by assimilating CO_2 emission from the environment.

Abstract. When temperature in the leaf gas exchange system changes, the thermodynamic parameters describing the condition of moist air also change. A temperature change of 1 °C in plant leaf tissues leads to a change in partial water vapour pressure of 144 Pa in the gas exchange cavities. Then a temperature decrease of 1 °C in a plant leaf produces 0.897 g of condensate, from 1 m^3 of air in leaf ventilation cavities on the surface. When the temperature of plant leaves in the leaf ventilation system changes, the total water vapor state on the inner surface of the leaves changes, and the water vapor state in the stomatal cavities changes. The thickness of the formed condensate film on the plant leaf canal wall surfaces depends on the canal diameter and temperature change. The paper presents information about the mechanism of water formation and thermodynamic processes in the plant leaf gas exchange system participating in the process of assimilation. The formation and change of the internal surfaces of the stomatal cavities of the water film sheet allow the participation of chemical processes in the assimilation of CO_2 emissions from the environment.

Keywords: CO_2 assimilation process, thermodynamics of a plant leaf, leaf gas exchange system, bionic leaf.

Introduction

The achievements of mankind in the field of new technologies have essentially changed living conditions on our planet and set new requirements for man himself. The current anthropogenic changes occurring in nature is the result of human activity and at the same time one of the greatest challenges to humankind. In nature they take place in all fields of human activities (Baltrėnas et al., 2008; Stravinskienė, 2009; Nobel, 1991; Zhang, 2015). The heaviest environmental anthropogenic pollution is caused by the burning of fossil fuels (coal, oil) in energy when heat, mechanical energy and electricity are produced. The anthropogenic pollution is a complex global problem encountered in all research fields while developing new technologies harmless to human health and preserving nature and its biological variety (Martin & Henrichs, 2010; Butkus et al., 2014; Shujie et al., 2015). In this respect it is particularly important to abate environmental pollution with CO_2 gas and produce biomass as the result of the energy efficiency of the assimilation process.

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No process in the physical world and in life can occur without movement. Therefore, the movement of CO_2 and metabolites between the plant leaf and the environment in the process of assimilation is only possible when a driving force is working. To create the driving force, energy is required. In a plant leaf, the share of the absorbed solar energy representing 98 to 96% is transformed into energy in the form of heat. Due to a small mass and biologically limited maximum temperature (58 °C) of their tissues thin plant leaves are not able to accumulate released heat. Therefore, the solar energy transformed into heat in plant leaves has to be released, in the form of heat and water vapour, into the environment as a metabolite. In the process of plant energy exchange with the environment low-value and low-potential heat released by plants into the environment continues to participate in the cycles of water and air circulation and forms climatic conditions on Earth. Scientists have long been interested in thermodynamic processes in plants (Stern, 1933), because the energy metabolism of the plant together with the assimilation process forms an important natural creation-restoration system, creating conditions for the existence of life on the Earth (Sirvydas et al., 2011a). In terms of thermodynamics, the plant is a bad user of the solar heat energy provided, in the form of rays, for the synthesis of organic compounds. Theoretically, the utilisation rate of the solar energy absorbed by plants for the production of organic matter could represent around 20 to 25%. In practice, only about 1 to 2% of the absorbed solar energy is used for photosynthesis (Šlapakauskas, 2006; Fitte & Hay, 2002). From another standpoint, the plant leaf is a unique, cheap and particularly complex laboratory. The plant is capable of utilising non-concentrated radiant energy from the Sun, creating organic matter, utilising the major part of technological pollutants emitted into the atmosphere, and supplying oxygen to the environment by creating conditions for life on Earth. Over a year the globe's vegetation assimilates around 640 billion tonnes of carbon dioxide and releases around 500 billion tonnes of free oxygen, thus reducing environmental CO_2 emissions, and transpires around 65 200 km^3 of water (Brazauskienė, 2004).

Plants exist in nature as open systems which uninterruptedly conduct metabolism and the exchange of energy with the environment. In order to ensure the exchange of CO_2 and metabolites during the productive stage of the assimilation process, it is particularly important to create and maintain intensive driving forces in the leaf ventilation system. The anatomical structure of a plant leaf suggests that complex thermodynamic and hydrodynamic processes take place in the plant leaf ventilation system. These processes can either stimulate or suppress biological processes in the leaf. The plant leaf ventilation system consists of leaf stomatal cavities a leaf surface area of 1 mm^2 from 50 to 400 units with nano, micro and mini channels in the mesophile (Šlapakauskas, 2006). Processes taking place in nano-, micro- and mini-channels are relevant in all fields of natural and technological sciences (Sirvydas et al., 2011a; Sajith et al., 2011). Research into these channels focuses on the properties of energy transporting fluids (Ide et al., 2007), their velocities in the channels (Sobhan & Garimella, 2003), the dependence of the internal boundary layer on channel parameters and (Sajith et al., 2011) heat exchange (Sobhan & Garimella, 2001; Boye et al., 2006). We have not found any data about thermodynamic processes taking place in biological and technical nano-, micro- and mini stomatal channels.

During a long way of its evolution the plant has, to the maximum extent, adapted to the natural conditions of its habitat. The anatomical structure of plant organs has maximally adapted to the biological processes inside them and environmental physical factors of the habitat. Plant leaf temperature and the difference of temperatures between the plant and the environment are those factors which can generate (or intensify) forces responsible for exchange between the plant and the environment (Sirvydas et al., 2011b). The leaf gas exchange system consisting of stomata, mini-, macro- and nano-channels forms among the spongy tissue cells in a plant leaf. The leaf gas exchange system takes a large surface area of mesophyll cells by which they have direct contact with air circulating in the gas exchange system. The ambient air is the main supplier of CO_2 for the process of assimilation. 90 to 95% of CO_2 together with the ambient air enters the spongy tissue of the leaf through open stomata; plant metabolites (O_2 and water vapour) are released into the environment also through open stomata (Šlapakauskas, 2006; Nobel, 1991). During the sunny day, a thermal stomata engine (the biological prototype of a heat engine) works in a plant leaf and generates mechanical energy at the expense of heat which intensifies the process of assimilation by activating leaf energy and gas exchange with the environment (Ūksas et al., 2016).

In the gas exchange system of a plant leaf the physical processes of heat and mass exchange with the environment take place through stomata. In leaf cavities the cell walls of ventilation system surfaces have contact with two different environments. From one side the cell wall has contact with the physical-gaseous environment (CO_2 gas included), from the other side the cell membrane has contact with the cytoplasm environment of biochemical state. In the plant cell cytoplasm membranes have the selective permeability of dissolved materials and regulates their movement between the environment and the cell. It is evident that the physical processes occurring in a plant leaf as well as CO_2 gas transformations from the gaseous-physical state to the biochemical state have been insufficiently examined (Šlapakauskas, 2006; Sirvydas et al., 2014). Quite different information is presented about the role of the anatomical structure of a plant leaf in the processes of gas (CO_2, O_2, H_2O vapour) and energy exchange between the leaf and the environment (Wang et al., 2010).

The purpose of the research is the analysis of the plant leaf gas exchange process in order to elucidate the mechanism of formation of aqueous medium in the leaf gas exchange system, CO_2 and O_2 gas transition from gaseous (physical) to biochemical (through chemical) and vice versa.

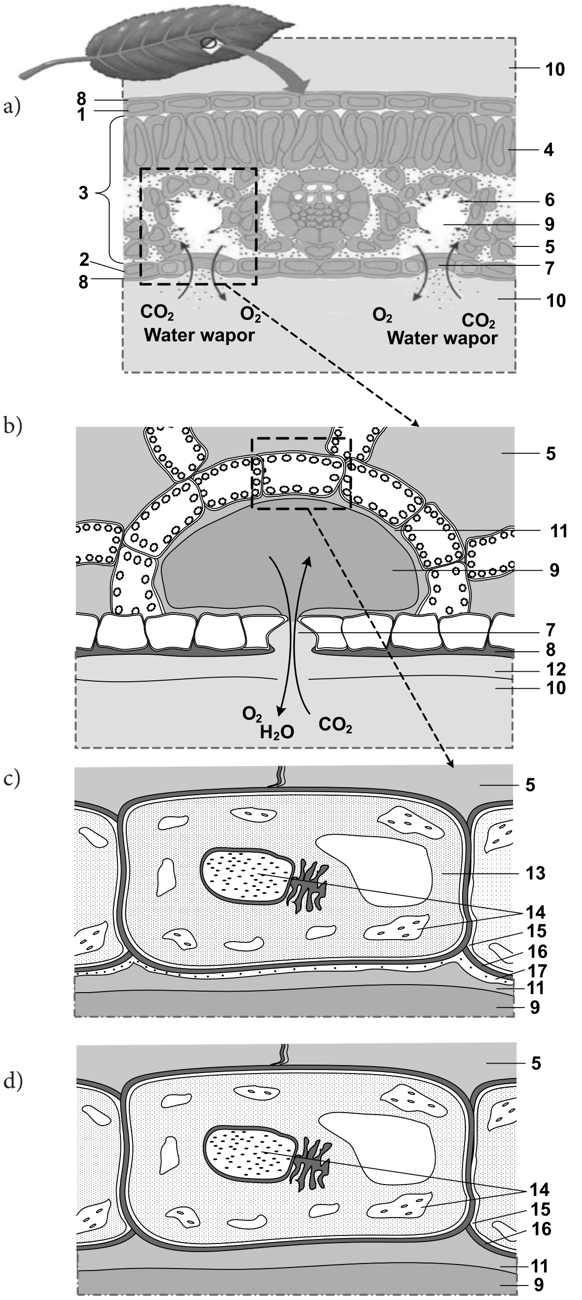
1. The structure and thermophysical model in the plant leaf gas exchange system

For bionic purposes plant leaf models are used to analyse the principles of vital activity in the leaf (Ye et al., 2013; Yuan et al., 2014; Sirvydas et al., 2013). Heat and mass exchange between the gaseous environment and the surfaces of a leaf occurs through the layer of transitional regimen which is also known as a internal boundary layer. Gas parameters therein gradually change from the parameters of the gaseous environment to those of the surface participating in the exchange (Sirvydas et al., 2011a; Incropera & DeWitt, 2001). This trend of physical processes applies to the surfaces of a plant leaf and other organs of the plant. The processes of heat and mass exchange with the environment in a plant leaf occur on the external and internal surface of a leaf. The process of assimilation involves both surfaces of a plant leaf with different environments and internal boundary layers of gaseous environments in which different heat and mass exchange processes occur.

The upper epidermis (1) and the lower epidermis (2) with the cuticle (8) cover the external surfaces of a plant leaf from the top and the bottom (Figure 1). 5 to 10% of CO_2 used in the process of assimilation diffuses through the epidermis and cuticle. The epidermis with cuticle nearly does not allow water vapour and gas to pass through (Šlapakauskas, 2006; Nobel, 1991). Consequently, the internal boundary layers of CO_2, O_2, H_2O vapour and other gas concentrations on the external surfaces of a plant leaf are unlikely to form. The external surfaces of a leaf participate in heat exchange with the environment; therefore they have the internal boundary layer of temperature on their surfaces (Šlapakauskas, 2006; Boye et al., 2006).

The internal surface of a plant leaf is in the spongy mesophyll layer of a leaf (5) (Figure 1a). The leaf gas exchange system of stomata (7), mini-, macro- and nano-channels is among the spongy tissue cells in a plant leaf. That forms a conditionally large contact cell area on the internal surface which has direct contact with the air circulating in the gas exchange system's mesophyll (9). The ratio between the area of the internal leaf surface (leaf ventilation system) and external leaf surface of plants exposed to shadow reaches 6.8–10.0, that of mesophytes – 11.0–20.0. In addition, the internal surfaces of a plant leaf evaporate the largest amount of water (80–98%) and release it into the environment through stomata (leaf ventilation system) (Šlapakauskas, 2006; Nobel, 1991).

The formation of the internal boundary layer of the leaf internal surface (Figure 1) is difficult to understand and experimentally immeasurable. It is natural because gas exchange processes take place in the system of leaf mini-, macro- and nano-channels, in the internal boundary layer (11) of leaf cell membrane (15) contact with gaseous environment (9). Metabolism and energy exchange on these cell surfaces take place when respective gradients participate. Engineering research in mini-channels shows the existence of the temperature internal boundary layer



1 – upper epidermis; 2 – lower epidermis; 3 – mesophyll; 4 – palisade tissue; 5 – spongy tissue; 6 – intercellular duct with the system of nano-, micro- and mini-channels; 7 – stoma; 8 – cuticle; 9 – gaseous environment in the spongy tissue of a leaf; 10 – ambient air around the leaf environment; 11 – internal boundary layer of the internal surfaces of a leaf; 12 – internal boundary layer of the external surface of a leaf; 13 – cytoplasm; 14 – cell organoids; 15 – cell membrane; 16 – cell wall; 17 – water vapour condensate formed on the external surface of a leaf

Figure 1. a – Chart of the plant leaf anatomical structure and gas exchange with the environment; b – Model of the internal boundary layer of the internal and external surfaces of a leaf (CO_2, O_2, H_2O vapour); c – Model of the internal boundary layer of the internal surface of a leaf when water condensate forms on a cell surface in the period of temperature drop; d – Model of the internal boundary layer of the internal surface of a leaf when water condensate evaporates from a cell surface in the period of temperature rise (Sage & Monson, 1999; Pirasteh-Anosheh et al., 2016)

and its dependence on the physical parameters of channels and fluids (Sajith et al., 2011; Sobhan & Garimella, 2001; Boye et al., 2006). Therefore, the internal boundary layers of temperature, CO_2, O_2, H_2O vapour and other gas concentrations may occur in the internal boundary layer of plant leaf internal surfaces (11). The internal internal boundary layer of a leaf participates in the process of CO_2 assimilation and is distinguished by a large number and variety of processes occurring inside it. In the internal boundary layer (11) of the leaf ventilation system CO_2 gas transits from the physical state to the biochemical level of a cell. A direct transition of CO_2 gas from the physical state to the biochemical level of a cell is unlikely. It is realistic that this CO_2 transition from the physical level to the biochemical level of a cell occurs with the help of chemical process. It is therefore necessary to analyse the thermodynamic processes in the internal boundary layer of the contact of plant leaf internal surfaces with the gaseous environment when plant leaf temperature changes.

2. The methods of research

The main object of research was research into the processes of exchange between the plant and the environment by applying the method of idealisation. This method involves the idealisation of the energy of biological processes occurring in a plant leaf as a means of discovering physical processes occurring in the plant leaf gas exchange system (in stomata with nano-, micro and mini-channels in the mesophyll) and in the layer of plant exchange with the environment during daylight hours when plant leaf temperature changes.

The temperature of a plant growing in natural environmental conditions was measured by thermocouple temperature sensors made of copper-constantan wires, 0.05 mm in diameter (Figure 2). The measurements were recorded with an instrument having a microprocessor data processing and accumulation system. Temperatures were recorded by necessity taking a maximum of 100 measurements per second.

Temperature sensors for all temperature measurements were used in observance of the requirements to be met by temperature measurements (in respect of the plant and its environment) (Sirvydas et al., 2006). The reliability of temperature measurements was evaluated by the describing the spread of values reasonably attributable to the temperature value concerned. The obtained total uncertainty of temperature measurements is 0.042 °C and relative uncertainty of temperature estimate – 0.07%, which corresponds to the confidence probability of 99% and demonstrates sufficient accuracy of temperature measurements.

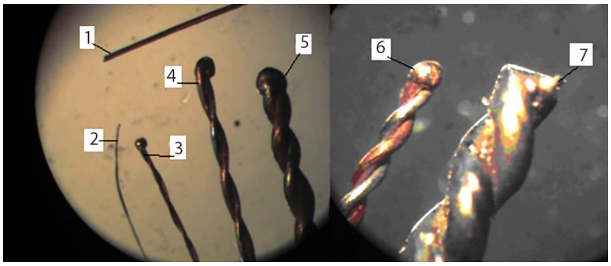


Figure 2. Individually manufactured temperature measuring sensors of various thicknesses: 1 – human hair 0.04 mm; 2 – temperature sensor 0.005 mm; 3 – sensor 0.03 mm; 4 – sensor 0.07 mm; 5 – sensor 0.18 mm; 6 – sensor 0.3 mm; 7 – factory sensor 0.45 mm

Measuring the local temperature of a heat-impermeable 1mm thick plant leaf plate is an extraordinary problem. It is not possible to measure the temperature at the apex of a plant leaf with a leaf surface area of up to 100 units / mm^2. The thermometer (sensor) does not show the temperature of the measured point, but the totality of its heat exchange with the environment.

3. Results of investigation

The local temperature of a plant leaf shows the total result of biological and energy exchange processes occurring in a leaf. Intensive metabolism and energy exchange in satisfying the needs of the assimilation process occur in a plant leaf during daylight hours. The satisfaction of the biological and physical environment needs of the assimilation process also depends on the processes taking place in the ventilation system of a plant leaf. We present the experimental measurement results of the temperature of a plant leaf and its surrounding which are useful for the analysis of thermodynamic processes in the plant leaf ventilation system.

In natural environmental conditions during daylight hours air temperature around the plant is continually changing and chaotically pulsating (Figure 3). Air temperature pulsations are created by the vertical airflows of unequal temperature in a phytocenosis and the temperature fields of energy exchange in plant organs.

Changing temperature around the plant (Figure 3), together with the change of the balance of plant energies, manifests itself in the local temperature through the process of plant leaf thermal accumulation. As theoretical studies show, a changing balance of energies in the plant can lead to variations in the local temperature of plant leaves (Sirvydas et al., 2011a). The measurements

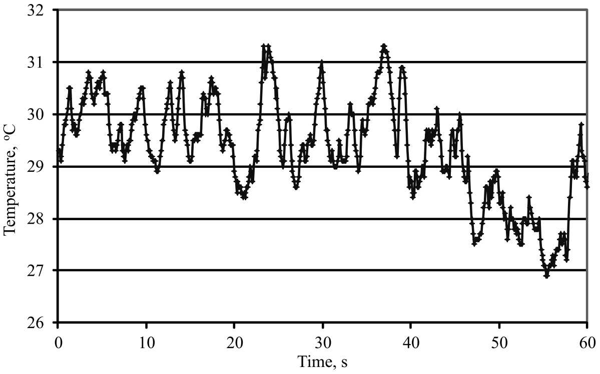


Figure 3. Temperature fluctuations in the air around the plant during the sunny period of the day under natural environmental conditions. Wind speed v_m = 1.1 m/s

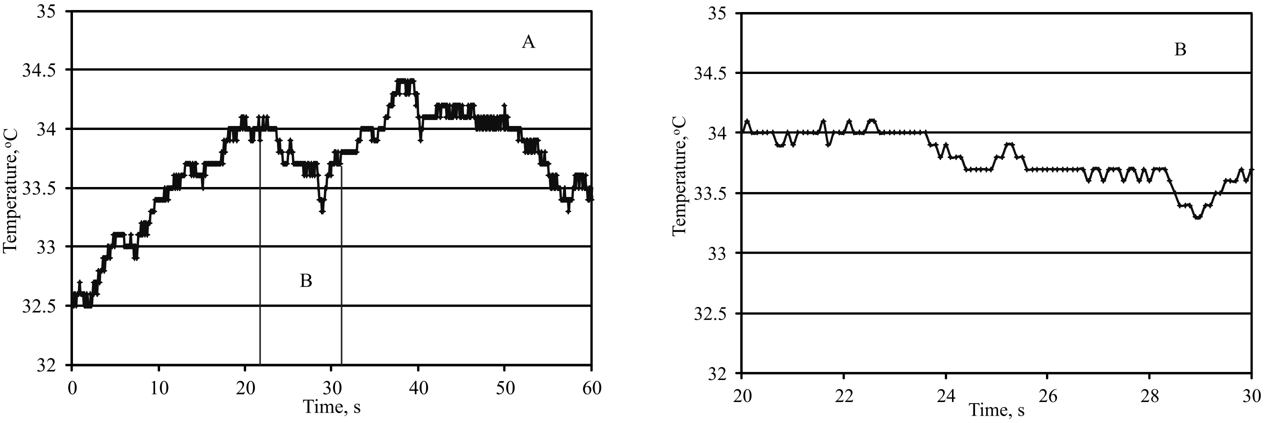


Figure 4. Temperature fluctuations in a plant leaf during the sunny period of the day under natural environmental conditions. Wind speed $v_m = 1.1$ m/s

of temperature around a plant leaf during daylight hours in natural environmental conditions are presented (Figure 4). A large quantity of reports on plant leaf temperature measurement (Figure 4a) did not highlight the thermal accumulation process of a plant leaf. Upon changing the timescale, a change in plant leaf temperature within an interval of 10 s is shown in Figure 4b.

Figure 4 the experimental plant leaf temperature's pulsations under natural environmental conditions are confirmed by our previous theoretical studies of the plant leaf energy balance equation and theoretical modeling of the processes. We present a theoretical equation for the energy balance of the plant leaf that allows to examine the temperature pulsations Δt in the plant leaf by estimating environmental and plant biological factors (Sirvydas et al., 2011b).

$$\Delta t = \left(2\left(t_0 - t_{apl}\right) + \frac{wr}{\alpha}\right)\left(1 - \exp\left(\frac{-\alpha S}{\rho c \delta} \cdot \tau\right)\right).$$

Temperature pulsations in the plant leaf occur during the processes of thermal accumulation of leaf tissues and heat exchange with the environment.

4. Discussion

When leaf temperature changes other parameters describing the state of gas in the leaf gas exchange (ventilation) system also change. Gases (CO_2, O_2, N_2 and others) in air content are in the state of superheated gas. In natural environmental conditions this gas in superheated state does not change the aggregate state in the leaf ventilation system; it remains superheated all the time. In natural environmental conditions water vapour in the plant leaf gas exchange system may change not only its aggregate state (gaseous↔liquid) but also the thermodynamic state of water vapour (moist↔saturated↔superheated vapour). Therefore while analysing the thermodynamic processes occurring in the system of plant leaf gas exchange (ventilation), it is necessary to observe the aggregate state of H_2O and evaluate the state of water vapour. In natural environmental conditions the plant leaf exchange may have all possible forms of H_2O (solid, liquid and gaseous) and states of water vapour (moist, saturated and superheated gas states in a mixture of gases). The evaluation of the water vapour state during leaf gas exchange is difficult as it requires complex observations and compatibility between the biological and thermodynamic processes taking place in the internal boundary layer of the leaf internal surface. Thermodynamic processes in the mixture of gases present in plant leaf ventilation cavities depends on the partial pressure of water vapour. When plant leaf tissue temperature changes, other parameters of the mixture of gases participating in the exchange also change. During daylight hours when leaf energy exchange with the environment takes place the change of the thermodynamic parameters of gases in the leaf gas exchange system first occurs in the internal boundary layer of gas contact with the surface. Since the leaf ventilation system consists of mini-, macro- and nano stomatal channels, changes in the state of water vapour occur in the internal boundary layer of the surface of plant leaf cell contact with the gaseous environment. Experimental research into thermodynamic parameters at the plant leaf cell level is not possible and we present, therefore, the theoretical analysis of thermodynamic processes occurring in the plant leaf gas exchange system by taking into account the thermodynamic trends of gas mixtures and water vapour.

During daylight hours when plant leaf temperature changes water vapour in the leaf gas exchange (ventilation) system changes its aggregate state and water vapour state j. That depends on the process of plant leaf temperature change. During the period of temperature rise the sequence of change of parameters for the H_2O gas component of the mixture of gases in the gas exchange system is: liquid → moist → saturated ($j = 100\%$) → superheated vapour ($j < 100\%$). During the period of leaf temperature drop the sequence of H_2O component parameter change is reverse. Essential changes in leaf energy exchange processes occur during these processes. The aggregate state of water changes, which leads to a change in volume of by around 1700 times. The values of heat transfer coefficient change by up to 1000 times.

For the numerical analysis of thermodynamic processes occurring in the plant leaf gas exchange system we assume that temperature in leaf cavities changes by up to 1 °C (19–20) °C. Based on the thermodynamics laws of moist air we state that when the temperature of plant leaf tissues decreases the process of moisture condensation on the surface of leaf gas exchange (ventilation) system walls will take place. Condensate will precipitate and moisten the surfaces of ventilation system cavities. A decrease of 1 °C in plant leaf tissue temperature will lead to a decrease in the partial pressure of water vapour in ventilation cavities by quantity Δp_g. The partial water vapour pressure in the state of full saturation at 20 °C is equal to 2337 Pa. Partial pressure at 19 °C is 2196 Pa. When plant leaf temperature changes by 1 °C, partial water vapour pressure in leaf ventilation cavities changes by quantity $\Delta p_g = p_{20}$ °C – p_{19} °C = 2337 – 2196 = 141 Pa. Once change in partial water vapour pressure Δp_g in the leaf ventilation system has been identified, the amount of condensate precipitation on the surfaces of leaf ventilation channels at a pressure of 98.1 kPa is determined. A change of 1 °C in plant leaf temperature produces 0.99 g of condensate from 1 m^3 of air on the surface of the walls in leaf stomatal channels ventilation cavities.

Further, we will analyse the dependence of the surface area of the plant leaf ventilation system on its volume. The system of leaf ventilation nano-, micro- and mini-channels is complicated. For the purpose of simplicity, we assume that the process of condensation takes place in ventilation cavities having a shape similar to a ball. The calculation data presented in Figure 5 show that the cavity volume (curve 1) increases more rapidly than the surface area (curve 2). This pattern shows that when the volume of plant leaf ventilation cavities increases (cavity diameter increases), thickness δ of the film of condensate having formed on cavity surfaces increases.

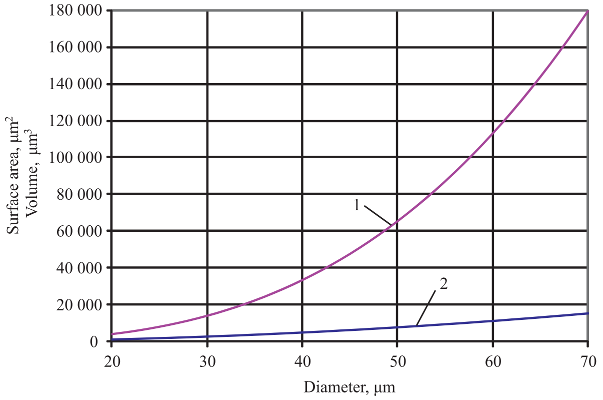


Figure 5. Dependence of the volume of cavities in the plant leaf ventilation system (curve 1) and the surface area of its walls (curve 2), on the channel diameter

Now, we determine the dependence of condensate film thickness δ on the volume of ventilation cavity. To that end, we assume that condensate uniformly distributes on the surface of ventilation cavities and forms a water condensate film of uniform thickness δ. Then, the easiest way to determine the dependence of condensate film thickness δ in ventilation cavities on cavity diameter *d* is to apply the ratio of cavity volume *V* to its surface area S. The thickness of condensate film for ball-shaped cavity $\delta = 0.149 \cdot 10^{-6} d$. For cylinder-shaped channel $\delta = 0.224 \cdot 10^{-6} d$. As we can see, the ratio of the volume of leaf ventilation channel cavity to its surface area *V/S* depends on cavity diameter *d*. The amount of condensate precipitated on cylindrically-shaped leaf channels is by 0.224/0.149 = 1.50 times thicker than that on ball-shaped channels. The thickness of the condensate film formed on the surface of plant leaf ventilation channel walls depends on cavity volume and temperature changes in plant leaf tissues and increases when they increase (Figure 6).

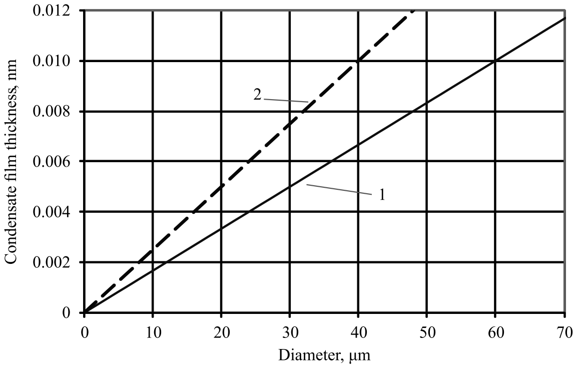


Figure 6. Dependence of condensate film thickness on the surfaces of cavity in the plant leaf ventilation system on the cavity diameter: curve 1 for a ball-shaped cavity; curve 2 – for a cylindrically-shaped channel when temperature changes by 1 °C

The thermodynamic analysis of the processes of formation of water medium on the internal surfaces of a leaf and gas exchange in the mini-, macro- and nano-cavities of a plant leaf has shown the following trends of leaf vital activities:

The CO_2 assimilation process in a plant leaf involves leaf's internal and external surfaces of different biological purpose with different internal boundary layers and different heat and mass exchange processes. When plant leaf temperature changes in the mixture of gases in the cavities of the leaf ventilation system, water vapour changes its aggregate state (gaseous↔liquid) on the internal leaf surface and the state of water vapour (moist↔saturated↔superheated vapour) in the cavities.

During daylight hours when leaf energy and mass exchange with the environment takes place in a leaf the change of the thermodynamic parameters first occurs in the internal boundary layers of gas contact with leaf surfaces. The essential changes in leaf energy and gas exchange processes occur when the aggregate state of water vapour and the state of water vapour change. They are seen in the cavities of the leaf internal surface, the internal boundary layer of the surface of contact of plant leaf cell with the gaseous environment.

In the internal internal boundary layer of a leaf CO_2 gas transits from the physical state to the biochemical level of a cell. A direct transition of CO_2 and O_2 gases from the physical state to the biochemical level of a cell is unlikely. It is realistic that the process of change of the water vapour aggregate state (gas↔liquid) participates in the exchange of CO_2 and O_2 gases between the physical state and the biochemical level of a cell in leaf gas cavities. The formation of water films on the internal surfaces of leaf cavities enables chemical processes to participate in CO_2 and O_2 exchange.

Conclusions

1. Under natural environmental conditions, on a sunny day, the air temperature washing the plant leaf and plant is chaotically pulsating.
2. As the leaf temperature of the plant changes, the water vapor in the leaf gas exchange (ventilation) system changes the physical state and condition parameters.
3. When the temperature of the plant leaf changes by 1 °C, 0.99 g of condensate falls on the surface of the walls of the leaf in the ventilation ducts of 1 m^3 of air.
4. A film of water condensate forms on the surface of the ventilation duct walls of the plant leaf. It depends on the change in cavity volume and temperature in the plant leaf tissues.
5. The water vapor codensate formed on the membrane's cell surfaces in the leaf's ventilation channels enables chemical processes to participate in the exchange of CO_2 and O_2 gases from the physical state to the biochemical level of the cell.

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