# COMPARISON OF ADSORPTION AND DESORPTION ISOTERIC HEATS FOR SOME GRAINS

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## ABSTRACT

The usual procedures for determining sorption isosteric heats by the application of the Clausius-Clapeyron equation to sorption isotherms of grains were examined. Isosteric heats of adsorption, desorption and total isotherms derived from various wheat, corn, rice and rapeseed cultivars were compared. There is no significant difference between adsorption and desorption isosteric heats of wheat. Isosteric desorption heats for shelled corn and rapeseed were considerable higher than those of isosteric adsorption heat. The differences between desorption and adsorption isosteric heats of shelled corn were larger at lower moisture contents, increasing from 2.6% at 0.14 mc to 5.1% at 0.05 mc. The differences between desorption and adsorption isosteric heats of rapeseed increased at lower moisture contents and ranged from 9.6% to 20.8% at 0.10 and 0.05 mc, respectively. Below the 0.11 mc, isosteric adsorption heats for rice were higher than isosteric desorption heat. The difference between adsorption and desorption isosteric heats of rice was 3.7% and 18% at 0.09 and 0.05 mc, respectively. Sorption isosteric heats for all studied crop species were found dramatically higher than those of total sorption isosteric heats.



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**Keywords:** Isosteric heat; Sorption isotherms; Wheat, Corn, Rice, Rapeseed, Grains, Clausius-Clapeyron equation

## INTRODUCTION

Current research on energy is directed toward efficient use of existing energy sources and increasing the potential uses of new and renewable sources. These same sources are of interest in drying crops and grains. Design of more efficient drying systems could be achieved by stating the correct mathematical models to estimate the heat and mass transfer mechanisms. It is essential to determine the energy required to remove moisture from agricultural crops (isosteric sorption heat) to complete the drying simulation model. Mainly two different methods are used to estimate the sorption isosteric heat. The most widely used method is the application of the Clausius-Clapeyron equation to sorption isotherms at different temperatures. The second method estimates the sorption isosteric heat by means of calorimetric techniques and of Riedel equation (Riedel, 1977; Sanjuan, et al., 1994; Sanchez, et al., 1997; Mulet, et al., 1999). This second method is based on thermal analysis, thermo-gravimetry, and differential-scanning calorimetry. It is noted that there is a good agreement between the isosteric sorption heat results of the calorimetric techniques and the Clausius-Clapeyron equation (Sanchez, et al., 1997; Mulet, et al., 1999).

The most commonly used calculation procedure for isosteric sorption heat is given below in detail (Gallaher, 1951; Labuza, 1968; Iglesias and Chirife, 1976; Cadden, 1988; Falabella, et al., 1989; Ayrancý, et al.,1990; Wang and Brennan, 1991; Tsami, 1991; Cenkowski, et al.,1992; Kiranoudis, et al.,1993; Rovedo, et al.,1993, Tolaba, et al.,1997; Sanchez, et al.,1997; Mulet, et al.,1999).

The isosteric sorption heat ($Q^{st}$) can be defined as a partial molar property, derived from the isotherm dependency on temperature (Mulet, et al., 1999):

$$\left[\frac{d\ \ln P}{dT}\right]_M = \frac{Q^{st}}{RT^2} \tag{1}$$

where $Q^{st}$ is the isosteric sorption heat (kJ/kg), $P$ is the partial pressure of water vapor (Pa), $R$ is the gas constant (kJ/kg K) and $T$ is the absolute temperature (K). From the above equation, applied to pure water, the following formula was obtained (Iglesias and Chirife, 1977; Sanchez, et al., 1997; Mulet, et al., 1999):

$$\left[\frac{d \ln a_w}{dT}\right]_M = \frac{Q_n^{st}}{RT^2} \tag{2}$$

where $Q_n^{st}$ is the net isosteric sorption heat (kJ/kg), $a_w$ is the water activity (decimal), $M$ is the moisture content (decimal d.b.). The net isosteric sorption heat ($Q_n^{st}$) represents the difference between the isosteric heat ($Q^{st}$) and free water vaporization energy ($L_r$). The net isosteric sorption heat ($Q_n^{st}$) can be calculated by plotting the sorption isotherms as ln($a_w$) at a specific m.c. versus 1/$T$ and measuring the slope which equals the -$Q_n^{st}$/R (Wang and Brennan, 1991). The application of this method requires the measurement of sorption isotherms at least three temperatures. The isosteric sorption heat may also be calculated from the integrated form of Equation 2 applied to sorption isotherms measured at two temperatures (Wang and Brennan, 1991):

$$Q_n^{st} = R\left[\frac{T_1 T_2}{T_2 - T_1} \ln \frac{a_{w2}}{a_{w1}}\right] \tag{3}$$



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Equation 2 is based on the assumption that ($Q_n^{st}$) is invariant or varies very little with temperature. Riedel equation can adequately describe the influence of temperature on water activity (Mulet, et al., 1999):

$$\ln\left[\frac{a_w(T_2)}{a_w(T_1)}\right]_M = A\exp(-bM)\left[\frac{1}{T_1}-\frac{1}{T_2}\right] \tag{4}$$

where $A$ and $b$ are the characteristic constants. Isosteric sorption heat can be calculated from the combined form of Equation 3 and Equation 4:

$$Q^{st} = Q_n^{st} + L_r = C\exp(-bM) + L_r \tag{5}$$

The purpose of the present work is to examine the application of Equation 2 to sorption isotherms of different agricultural crops and to compare the calculated isosteric sorption heats using the adsorption, desorption, and total isotherms.

## MATERIALS AND METHODS

### Materials

Equilibrium moisture data were obtained from the literature as indicated below; these data correspond to three or four different temperatures (Table 1). Barley, yellow dent corn, rough rice, drum wheat, soft wheat and hard wheat (ASAE, 1994); adsorption, desorption and total isotherms for wheat, shelled corn, rice and rapeseed (Sun, 1998).

### Methods

Equilibrium relative humidity of these crops was estimated by various equations as suggested by ASAE (1994) and Sun (1998). These equations are given below:

1. Chung Equation

$$h_r = \exp\left[\frac{-C_1}{T + C_2}\exp\left(-C_3\ M\right)\right] \tag{6}$$

2. Modified Halsey Equation

$$h_r = \exp\left[-\exp\left(C_1 + C_2 T\right)M^{-C_3}\right] \tag{7}$$

3. Modified Oswin Equation

$$h_r = \frac{1}{1 + \left(\frac{C_1 + C_2 T}{M}\right)^{C_3}} \tag{8}$$

4. Strohman-Yoerger Equation (Sun, 1998)

$$h_r = \exp\left[C_1 \exp\left(-C_2 M\right)\ln P_s - C_3 \exp\left(-C_4 M\right)\right] \tag{9}$$

where $h_r$ is the relative humidity (decimal), $T$ is the temperature (°C), $M$ is the moisture content (% d.b.), $P_s$ is the saturated vapor pressure (Pa), $C_1$, $C_2$, $C_3$ and $C_4$ are equation constants.

The net isosteric sorption heat was determined using the Equation 2 by plotting the ln $a_w$ *versus* $1/T$ at certain moisture contents and measuring the slope which equals the $-Q_n^{st}/R$. Then the calculated average latent heat of vaporization energy for free water (2450.9 kJ kg$^{-1}$ for 0 to 50°C and 2429.1 kJ kg$^{-1}$ for 5 to 80°C) was added to these $Q_n^{st}$ values. Equation 5 was used to determine the interaction between the $Q^{st}$ and crop moisture content. The coefficients, $C$ and $b$, were determined by applying the non-linear regression techniques to the isosteric heats and crop moisture contents. Table 1 gives the coefficients of Equation 6 to 9, $C_1$, $C_2$, $C_3$ and $C_4$, required to calculate the equilibrium relative humidity.

## RESULTS AND DISCUSSIONS

The data from sorption isotherms for all studied crops at different temperatures were plotted according to Equation 2. Slopes of the lines and $Q_n^{st}$ values were determined by regression and used to compute C and b (Table 2).

Fig. 1 gives the influence of moisture content on the wheat sorption isosteric heat determined from adsorption and desorption isotherms of various wheat cultivars. It can be noted that there is no significant difference between adsorption and desorption isosteric heats for wheat.

Figure 2 shows the influence of moisture content on the sorption isosteric heats of shelled corn, rice and rapeseed determined from adsorption and desorption isotherms. Isosteric desorption heats of shelled corn were higher than those of isosteric adsorption heats. The differences between desorption and adsorption isosteric heats of shelled corn were larger at lower moisture contents, increasing from 2.6% at 0.14 mc to 5.1% at 0.05 mc.

Isosteric desorption heats of rice were higher than those of isosteric adsorption heats above 0.11 mc. Below the 0.09 mc., isosteric adsorption heat increased rapidly. The difference between adsorption and desorption isosteric heats was 3.7% and 18.0% at 0.09 and 0.05 mc., respectively.

Isosteric desorption heats of rapeseed were higher than those of isosteric adsorption heats. The differences between desorption and adsorption isosteric heats for rapeseed increased at lower moisture contents. This difference was 9.6 and 20.8% at 0.10 and 0.05 mc., respectively.

Figure 3 shows the sorption isosteric heat difference among the several wheat cultivars and wheat total isotherms. Above 0.20 mc., all wheat cultivars have very low isosteric heats which are close to the latent heat of vaporization of free water. Below 0.20 mc., there is an increase of sorption isosteric heats for soft and hard wheat. At 0.10 mc., isosteric sorption heats for soft wheat, hard wheat and durum wheat were calculated as 3351 kJ $kg^{-1}$, 3166 kJ $kg^{-1}$ and 2789 kJ $kg^{-1}$, respectively. Isosteric sorption heat for wheat total was remained close to latent heat of vaporization of free water.

Figure 4 shows the sorption isosteric heat difference between the yellow dent corn and shelled corn total isotherms. Above 0.20 mc., there is no difference between the isosteric sorption heat for yellow dent corn and shelled corn total. Below 0.20 mc., there is an increase of sorption isosteric heat of yellow dent corn. At 0.10 mc., isosteric sorption heats of yellow dent corn and shelled corn total were calculated as 3391 kJ $kg^{-1}$, 2882 kJ $kg^{-1}$, respectively; a difference of 15 %. Since the ASAE data (ASAE, 1994) do not indicate chemical composition of the yellow dent corn and shelled corn, it is difficult to analyse sorption isosteric heat results. However, yellow dent corn is the open-pollinated corn used before hybrids were introduced, while the shelled corn is hybrid cultivars. Therefore, these differences could be attributed to the physicochemical properties of corn cultivars used to determine the equilibrium moisture content equilibrium relative humidity relationships.

Figure 5 shows that the sorption isosteric heat difference between the rough rice and rice total isotherms. At 0.14 mc., there is no significant difference between the isosteric sorption heat of rough rice and rice total. Below 0.14 mc., there is an increase in sorption isosteric heat of rough rice. At 0.10 mc., isosteric heat of sorption values of rough rice and rice total were calculated as 3346 kJ $kg^{-1}$, 3086 kJ $kg^{-1}$, respectively; a difference of 7.8%. It must be noted that the rough rice includes the fibrous hull, while rice has de-hulled form. Therefore, these differences could be attributed to the physical form of the grain used to determine the equilibrium moisture content equilibrium relative humidity relationships.

## CONCLUSIONS

It may be concluded that isosteric desorption heats of grains generally tend to be higher than those of adsorption isosteric heats. Total isosteric heats of grains determined from the mean value of adsorption and desorption isotherms were dramatically lower than those of special grain cultivars. Therefore total or average sorption isotherms for grain cultivars could not adequately describe their real sorption characteristics. Since water sorption isotherms depend on the material properties such as variety, pre-treatment, harvest time and climatic conditions, their determination seems to be necessary, to obtain the most accurate isosteric sorption heat data.

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Table 1 Coefficients, $C_1$, $C_2$, $C_3$ and $C_4$, for Eq. 6 to 9 (ASAE, 1994; Sun, 1998)

| Crop | | Eq. No. | Constants | | | |
|---|---|---|---|---|---|---|
| | | | $C_1$ | $C_2$ | $C_3$ | $C_4$ |
| Barley | | 6 | 761.66 | 91.323 | 19.889 | |
| Yellow dent corn | | 6 | 312.3 | 30.205 | 16.958 | |
| Rough rice | | 6 | 594.61 | 35.703 | 21.732 | |
| Durum wheat | | 6 | 921.65 | 112.35 | 18.077 | |
| Hard wheat | | 6 | 529.43 | 50.998 | 17.609 | |
| Soft wheat | | 6 | 726.49 | 35.662 | 23.607 | |
| Wheat | (ads.) | 6 | 401.52 | 73.607 | 0.14974 | |
| | (des.) | 6 | 545.25 | 64.047 | 0.17316 | |
| | (total) | 6 | 478.87 | 64.933 | 0.16558 | |
| Rapeseed | (ads.) | 7 | 2.7812 | $-8.9162 \times 10^{-4}$ | 1.6685 | |
| | (des.) | 7 | 2.8989 | $-1.4596 \times 10^{-2}$ | 1.5454 | |
| | (total) | 7 | 2.8380 | $-9.6915 \times 10^{-3}$ | 1.5845 | |
| Shelled corn | (ads.) | 8 | 13.1882 | -0.058628 | 2.98726 | |
| | (des.) | 8 | 13.9005 | -0.076819 | 2.96243 | |
| | (total) | 8 | 13.7738 | -0.074127 | 2.96856 | |
| Rice | (ads.) | 9 | 2.60693 | 0.22350 | 8.48875 | 0.19608 |
| | (des.) | 9 | 1.03151 | 0.13755 | 7.73688 | 0.17268 |
| | (total) | 9 | 1.15668 | 0.15345 | 7.78269 | 0.17828 |

ads., adsorption isotherm; des., desorption isotherm; total, mean value obtained form adsorption and desorption isotherms

Table 2. Derived Coefficients for Eq. 5 and Valid Temperature and Moisture Ranges

| Crop | | Coefficients | | Temperature range (°C) | Moisture range (decimal, d.b.) |
|---|---|---|---|---|---|
| | | *C* | *b* | | |
| Barley | | 2391.31 | 19.83 | 0-50 | 0.09≤ *M* ≤0.22 |
| Yellow dent corn | | 5130.87 | 16.94 | 0-50 | 0.10≤ *M* ≤0.24 |
| Rough rice | | 7757.09 | 21.70 | 0-50 | 0.10≤ *M* ≤0.14 |
| Durum wheat | | 2034.64 | 17.96 | 0-50 | 0.10≤ *M* ≤0.26 |
| Hard wheat | | 4141.52 | 17.57 | 0-50 | 0.10≤ *M* ≤0.26 |
| Soft wheat | | 9486.29 | 23.54 | 0-50 | 0.10≤ *M* ≤0.20 |
| Wheat | (ads.) | 111.15 | 13.97 | 0-50 | 0.10≤ M ≤0.25 |
| | (des.) | 155.98 | 16.18 | 0-50 | 0.10≤ M ≤0.25 |
| | (total) | 137.24 | 15.46 | 0-50 | 0.10≤ M ≤0.25 |
| Rapeseed | (ads.) | 152.49 | 20.62 | 5-80 | 0.05≤ M ≤0.25 |
| | (des.) | 1774.24 | 18.45 | 5-80 | 0.05≤ M ≤0.25 |
| | (total) | 1300.15 | 19.17 | 5-80 | 0.05≤ M ≤0.25 |
| Shelled corn | (ads.) | 990.91 | 10.60 | 0-50 | 0.05≤ M ≤0.24 |
| | (des.) | 1245.78 | 10.29 | 0-50 | 0.05≤ M ≤0.24 |
| | (total) | 1213.86 | 10.36 | 0-50 | 0.05≤ M ≤0.24 |
| Rice | (ads.) | 6147.32 | 21.64 | 0-50 | 0.05≤ M ≤0.24 |
| | (des.) | 2419.38 | 12.95 | 0-50 | 0.05≤ M ≤0.24 |
| | (total) | 2703.41 | 14.48 | 0-50 | 0.05≤ M ≤0.24 |

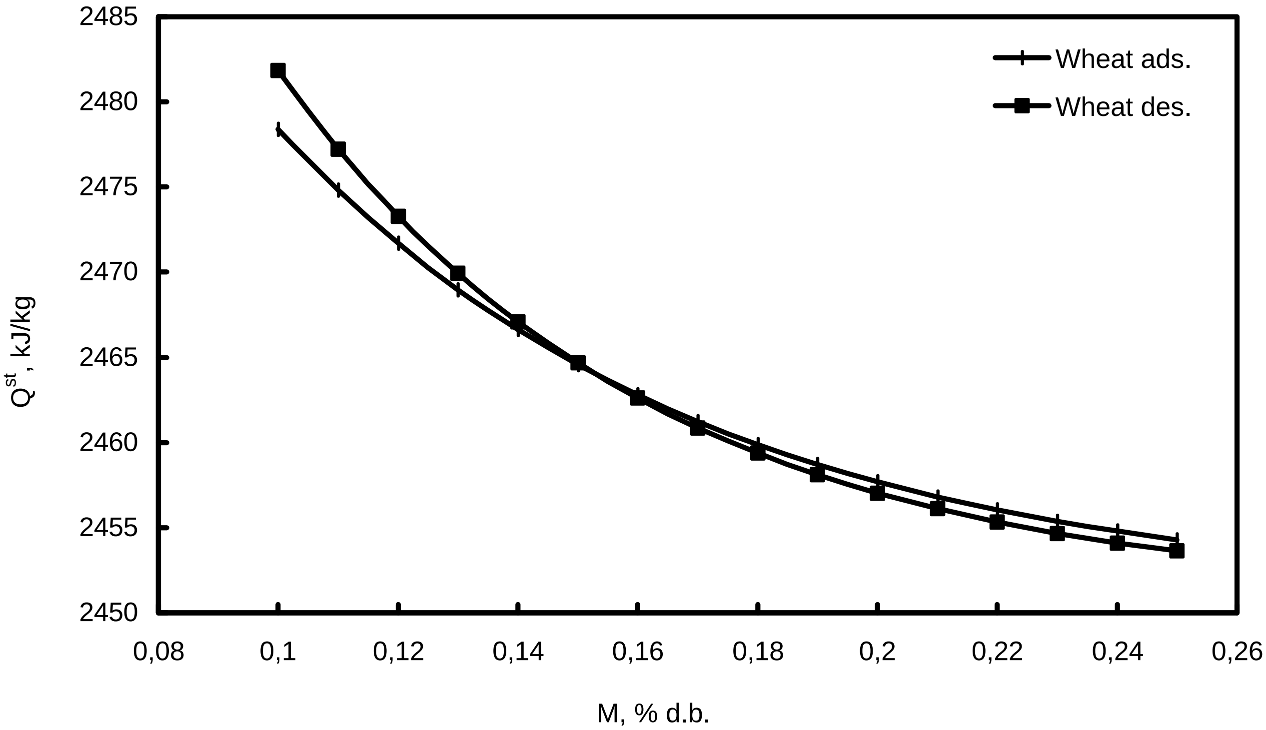


Fig. 1. Comparison of adsorption and desorption isosteric heat for wheat

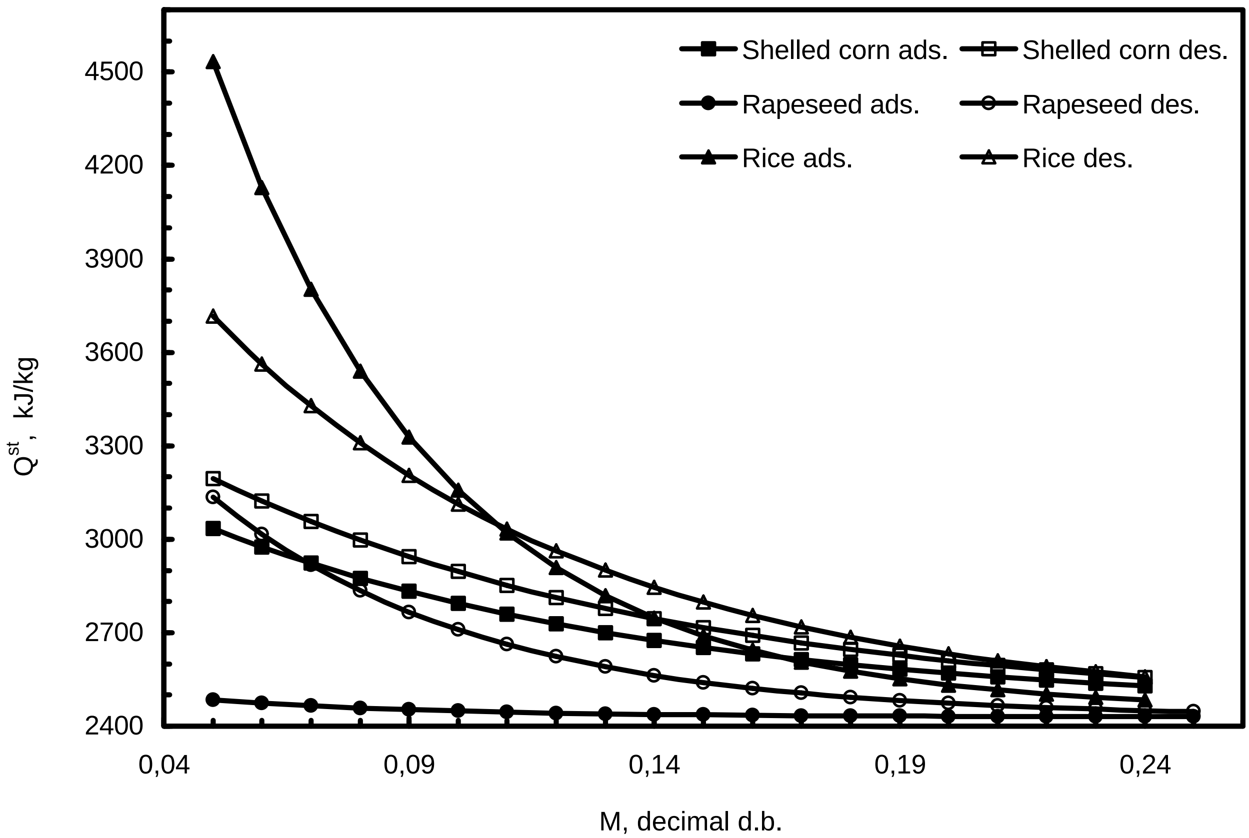


Fig. 2. Comparison of adsorption and desorption isosteric heat for main crops

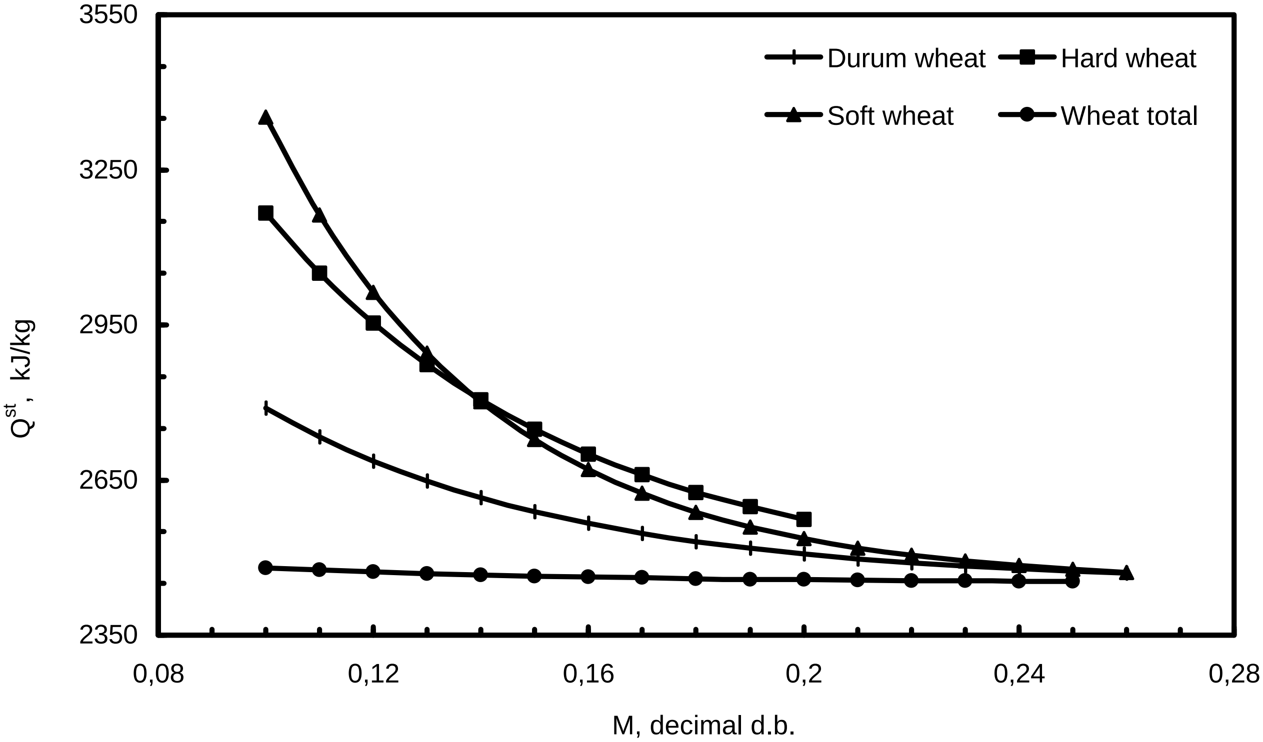


Fig. 3. Sorption isosteric heats for several wheat cultivars and wheat total isotherms

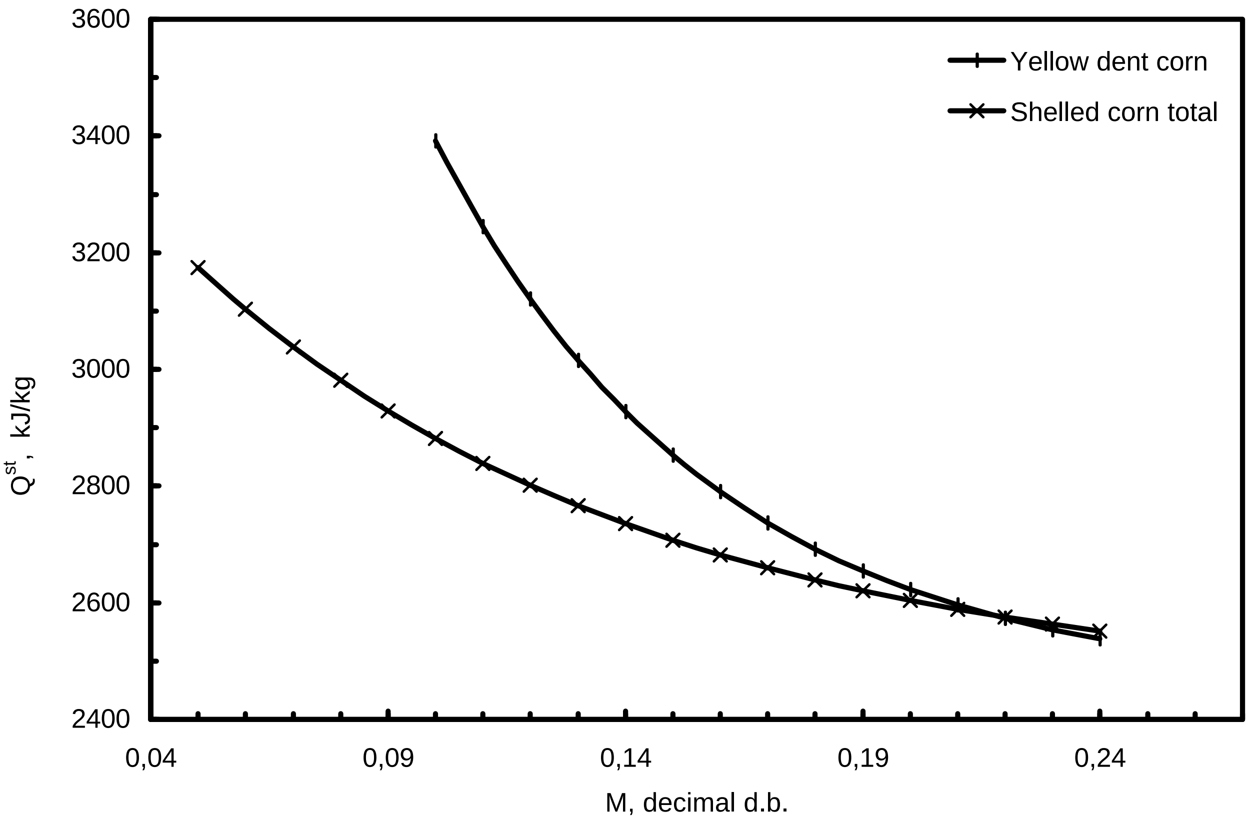


Fig. 4. Sorption isosteric heats of yellow dent corn and shelled corn total isotherms

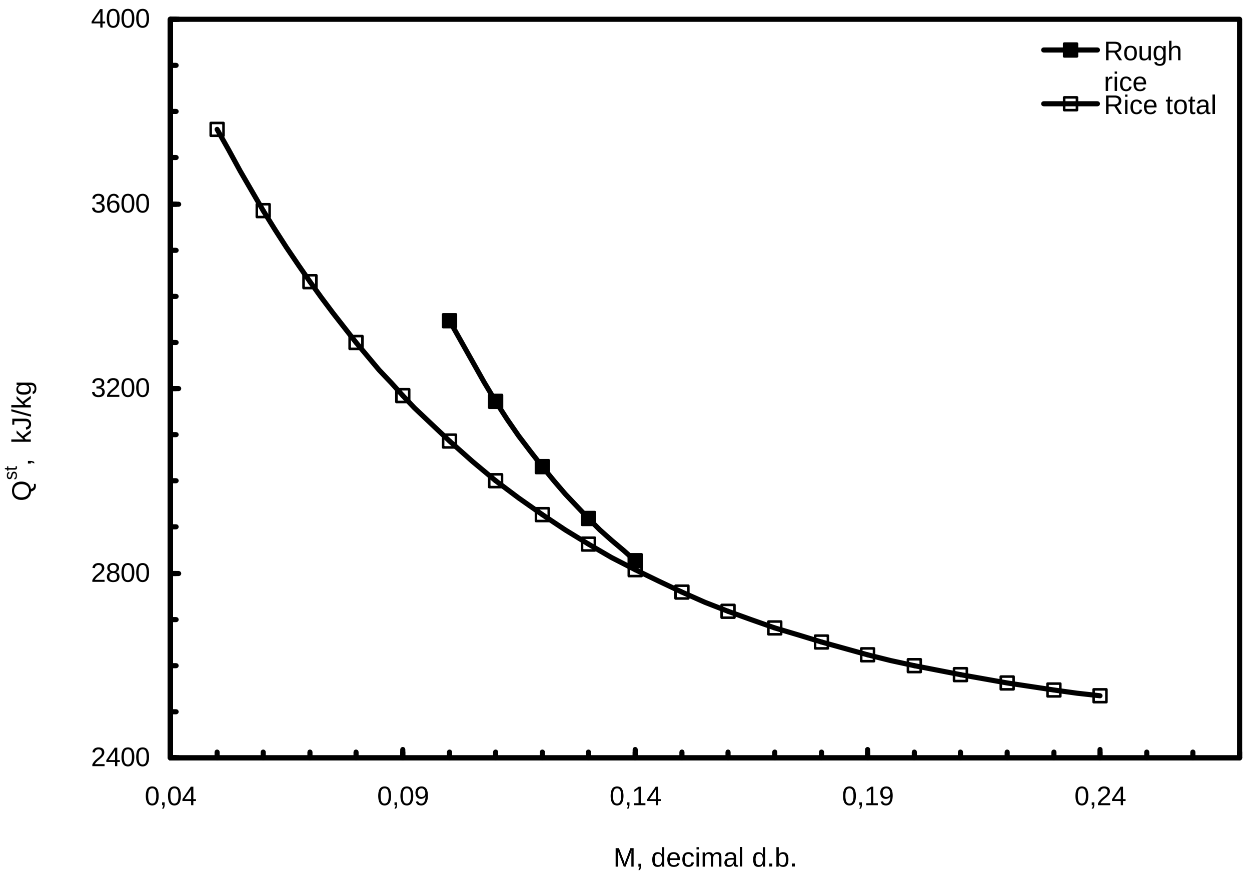


Fig. 5. Sorption isosteric heats of rough rice and rice total isotherms