Process innovation in the sugar industry: chromatographic sugar separation using SMB technology

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Summary

Chromatographic separation of sugar from raw juice is identified as a promising alternative for the current chemical purification process. The alternative process is based on chromatographic removal of sucrose from raw juice. Simulating moving bed technology (SMB) is chosen as the most suitable technology on the basis of purification level, limited degree of dilution and increased sugar yield. Experiments - up to the level of pilot scale - and process modelling are used hand in hand to develop the new process.

The selection of a suitable adsorbent is a key factor in designing a technically and economically feasible process. An adsorbent is selected which binds sucrose selectively compared to glucose, glutamine and betaine. The binding mechanism on a molecular scale (CH-π interaction) is weak enough to allow for a sensible desorption strategy. Sorption isotherms and mass transfer coefficients are fitted using experimental data. An SMB process model is used to evaluate the performance of the adsorbents.

The unit operations before (clarification and stabilisation) and after the SMB unit (evaporation and crystallization) as well as the utilization of process water streams are also taken into account. Experiments on lab-scale are carried out using microfiltration and reverse osmosis. SMB experiments are carried out on pilot scale using the selected adsorbent. A temperature swing is used, resulting in a concentration step during adsorption/desorption. This lowers the energy costs for water evaporation prior to the crystallization process.

The process is economical feasible when all identified savings are realised. Important issues are the reduction of sugar losses in the total process, a higher sucrose yield in the crystallization as a result of a higher purity, and limited operational costs due to prevented dilution.

Background

To obtain pure sugar from an aqueous sugar solution, crystallization is a commonly applied technique. However, the purifying power of crystallization is hindered with feeds that contain a relatively large amount of impurities. In those cases the feed needs to be purified prior to crystallization in order obtain a pure sugar. Figure 1 shows a schematic drawing of the general conventional method for the production of sucrose from sugar beets.

A so-called raw juice is obtained by extracting the soluble material from the beets with hot water. The raw juice which contains sucrose, non-sucrose compounds and water, is partially purified to remove a significant portion of the non-sucrose fraction. The most commonly used purification method is based upon the addition of lime and carbon dioxide (liming and carbonation, see figure 1). During these process steps various non-sucrose compounds are removed or transformed by reaction with the lime or by absorption on a calcium carbonate precipitate. The precipitate is usually removed by settling clarifiers or by appropriate filters. Conventionally, the calcium oxide and the carbon dioxide are produced by heating lime rock (calcium carbonate) in a high temperature kiln. The resulting used lime from the purification (so-called carbonation mud) is difficult to dispose of and contains about 20-30% of the original raw juice non-sucrose. Following the purification steps described, the remaining juice is referred to as thin juice.

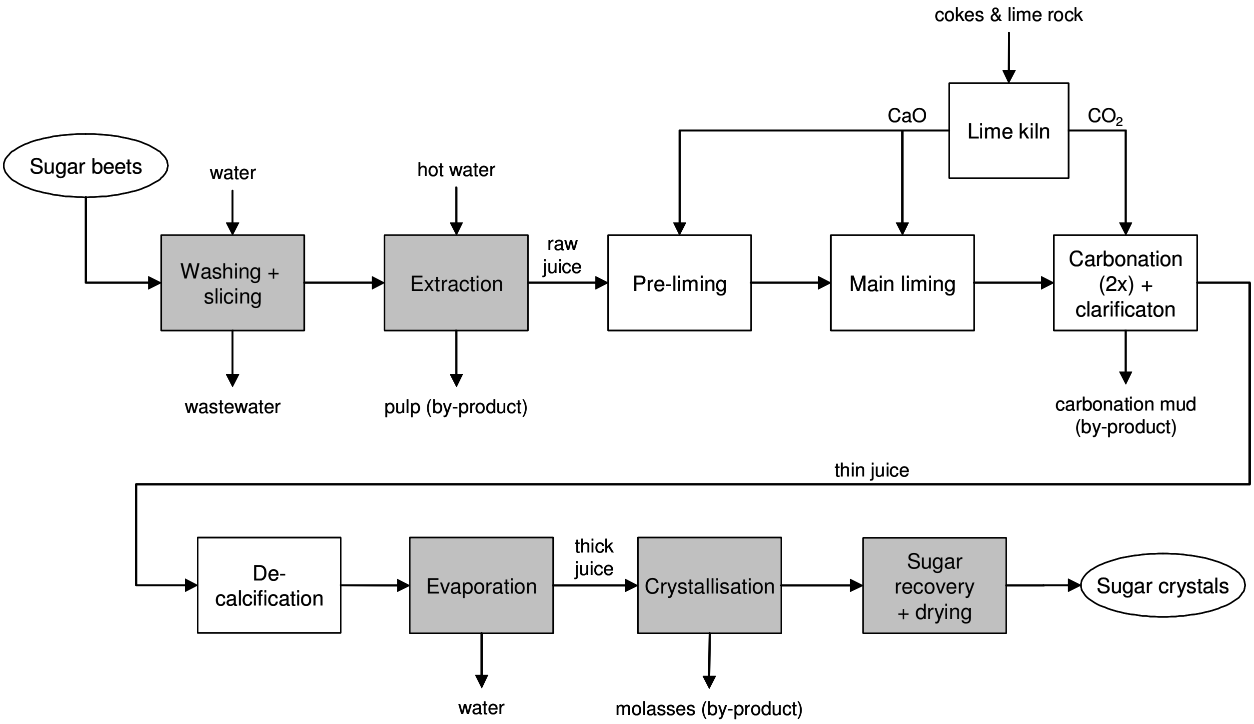

Figure 1 Conventional method for the production of sucrose from sugar beets.

The thin juice, which may range typically from about 15 to 20% solids, based upon the weight of the juice, is sent to an evaporative concentration step to raise the solids content to about 60-70% by weight (so-called thick juice). During the crystallization process it is not feasible to crystallize all of the sucrose in the thick juice as acceptable product. A large amount of this sucrose is lost to a discard called molasses. This inefficiency is largely due to the reality that the liming and carbonation purification procedures actually remove only a minor portion of the non-sucrose compounds in the juice. The presence of residual non-sucrose in the thick juice significantly interferes with the efficient crystallization and recovery of the sucrose. Consequently, a low value molasses is an unavoidable byproduct of the crystallization procedure.

Concluding, the conventional production of crystallized sucrose suffers from several disadvantages, which are in short: lime and CO_2 request great amounts of limestone and cokes, a complex multi-step process, large amounts of waste products and a restricted purity of the thin juice, urging for complex re-crystallization schemes, altogether resulting in an inefficient process with high costs. Other disadvantages are smell emissions and high-energy consumption.

In literature several improvements can be found on the process for purifying the raw juice from sugar beets, outlined above. A US patent (US5466294) for instance proposes a process, which involves subjecting the raw juice to a softening procedure, whereby more than half of the non-sucrose constituents can be removed. Thereupon the soft raw juice is concentrated and subjected to a chromatographic separation procedure, which utilizes an ion exchange resin as a chromatographic medium. The process, however, has the serious disadvantage that, due to the rather strong dilution, great amounts of water have to be removed during the juice thickening process. Moreover, a substantial amount of energy is needed for this process, making the process uneconomical.

US4968353 shows another method for refining sugar liquor by the mineral cristobalite and an ion exchange resin. Cristobalite exhibits specific adsorbent properties for various colloidal or suspended substances, while the ion exchange resin exhibits decoloring and desalting properties with respect to colorants and salts. By combining cristobalite and ion exchange even a non-washed sugar liquor like raw juice may be refined.The process, however, is based on ion exchange, which has a serious disadvantage that the process needs acids and bases to regenerate the resins.

Towards a new sugar process

In this paper an improved method is presented for refining raw juice (or any other liquor containing mono, di, tri or oligosaccharides). The juice is contacted with an adsorbent, which is fit or adapted to accumulate (by adsorption) the relevant saccharides on its internal surface. The adsorbent has been selected on the basis of its capability of CH-π interaction and, optionally, hydrogen bonding. Moreover the adsorbent has a high internal surface area.

As most saccharides are very hydrophilic, the choice for a relatively hydrophobic adsorbent (compared to ion exchangers) is rather surprising. The choice, however, is based on an observation in a quite different area: it is known that proteins in taste buds or receptors in addition to hydrogen bonding groups have aromatic groups that contain π-electrons for binding with saccharides (Kier, 1972). The involvement of aromatic groups suggests that CH-π interaction is important (Nishio *et al.*, 1995). The same interaction, optionally completed with formation of (a) hydrogen bridge(s), is used here to bind saccharides. It is emphasized that the adsorbent is fit to accumulate saccharides on its surface by (physical-chemical) adsorption, while the methods and systems found in literature make use of ion exclusion or ion exchange.

The resin selected in the experiments was Amberchrom, for which the sorption isotherms for sugar and main contaminations (glucose, glutamine and betaine) were determined.To take full economical advantage of the adsorbent characteristics, sucrose desorption is brought about by using a desorption liquid with a temperature higher than the feed temperature. To accumulate sucrose, the feed is contacted with the adsorbent's surface at a low temperature (35℃), while, to desorb (collect) the accumulated sucrose, the adsorbent's surface is heated to 95℃. Using the experimental set-up (shown in figure 2), the possibilities to increase the sucrose concentration by applying a temperature swing were examined. Results are given in figure 3 which shows adsorption and desorption breakthrough curves of sucrose from column experiments with raw juice. The sucrose concentration in the hot eluent is clearly higher than 1 ($C/C0 = 1.04$), which proves that the column not only adsorbs but also concentrates sucrose.

At a plant scale heating of the adsorbent will be carried out using a hot desorption liquid. As the proposed process is based on adsorption (not based on ion exclusion or ion exchange), a temperature swing can be used to collect sucrose. Due to using the temperature swing as proposed here, the resulting concentration is rather high, thus improving the process efficiency and effectiveness and lowering the process costs for juice thickening.

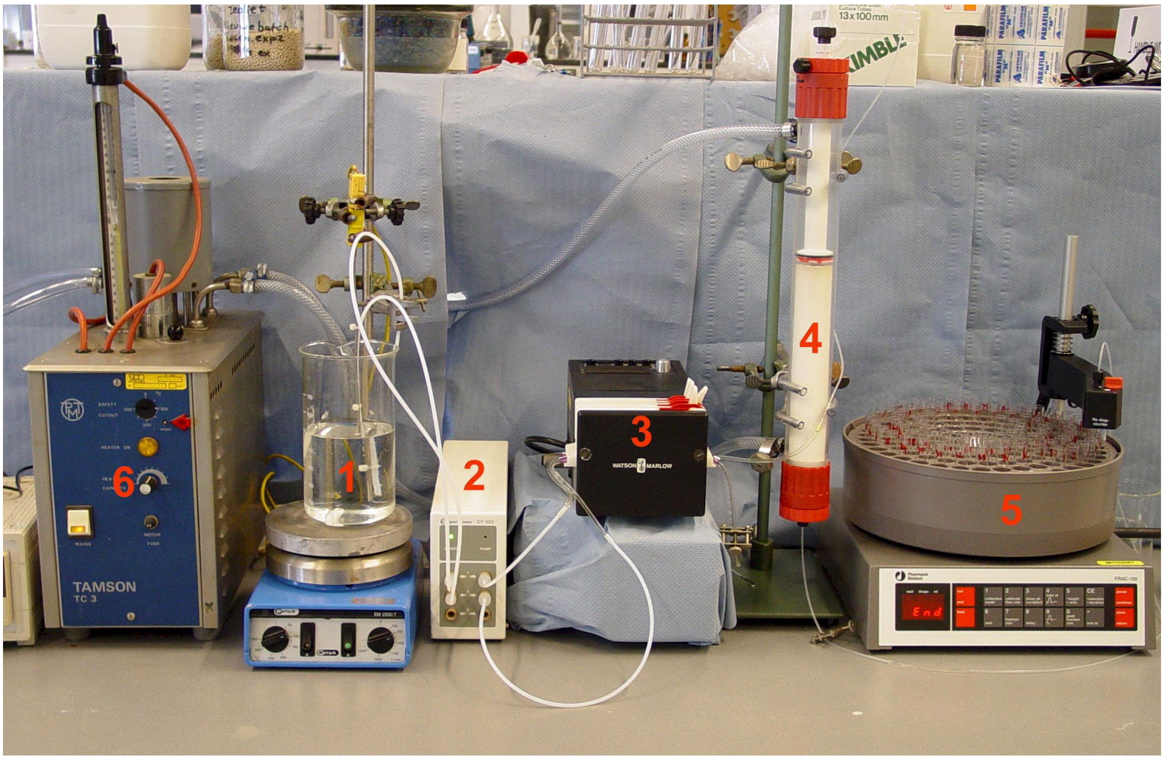

Figure 2 Laboratory set-up for adsorption/desorption experiments with Amberchrom (1: feed/eluens, 2: degasser, 3: pump, 4: column with water jacket, 5: fraction collector, 6: waterbath).

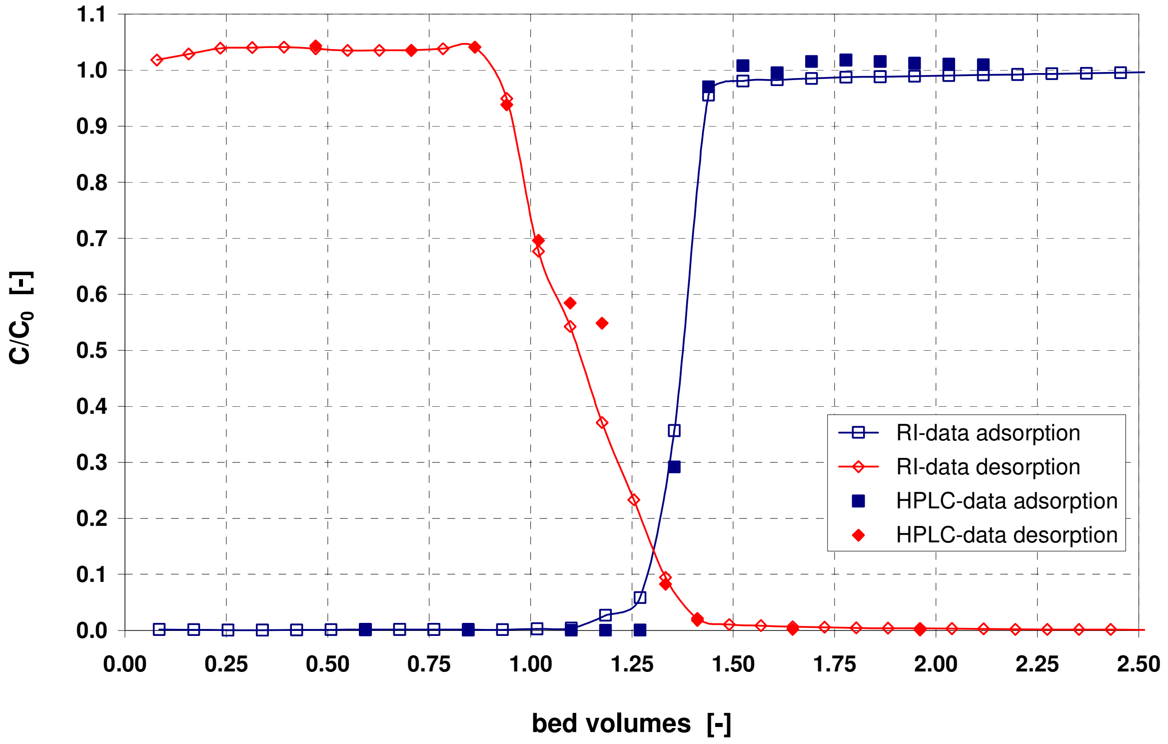

Figure 3 Sucrose concentration profiles in a raw juice adsorption/desorption experiment (adsorption: 35℃, desorption: 95℃).

Pre-treatment

Before the raw juice can be applied to the adsorptive separation step undissolved contaminations must be removed which otherwise would result in plugging the adsorption columns. In addition the juice must be microbial stable. The required pre-treatment is much more straightforward than in the current process. Three routes were evaluated experimentally:

- pre-liming (with or without the first carbonation step) and filtration;
- filtration (60 μm) and microfiltration (MF);
- filtration (60 μm) and heat treatment (plate heat exchanger).

The first route did not result in a clear juice and was abandoned. The second and third route both resulted in a microbial stable thin juice with only small particles, a final decision on the best pre-treatment method is still to be made. Several MF membranes were tested (pore size, flux). A flux of 100 kg/m^2/hr/bar was realised, with a maximum recovery of 90% and a loss of sucrose of 10%. This loss of sucrose can be further reduced to less than 4% by applying diafiltration or even lower by using a pateurizer (plate heat exchanger) instead of a microfiltration unit. The small particles still present in the stream did not negatively influence the performance of the adsorption unit.

The adsorptive separation unit

In the adsorptive separation step sucrose is adsorbed by the adsorbent and desorbed by eluting with water. The selected process unit-operation is a simulated moving bed (SMB) chromatographic process. SMB chromatography has been widely commercialised amongst others for the separation of glucose and fructose, and the desugarisation of molasses (Ruthven, 1984; Wankat, 1986). The experimental set-up is shown in figure 4.

Utilization of process water streams

During the adsorptive removal of sucrose a relative large waste stream containing invert sugars and non-sugars in low concentrations is obtained. A large part of the water is recovered using reverse osmosis and is reused as eluent in the adsorption unit. The size of the watery process stream is reduced with a factor 4-5 and contains 10% dry matter. Utilisation of this stream is subject for further investigation.

Process feasibility

Figure 5 shows a block diagram of a beet sugar refining process, incorporating the novel process steps as outlined above.

Raw juice from sugar beet or sugar cane is fed to the sugar plant. This raw juice contains sucrose but also colloidal or suspended solids, microorganisms, and dissolved inorganic and organic components like salts, organic acids, and invert sugars. Prior to the adsorptive purification of the juice, the feed is clarified and stabilised. Subsequently, this treated raw juice is brought into contact with an adsorbent, which is fit to accumulate sugar on its surface. This is carried out in an SMB chromatographic unit. The feed of the SMB is at a temperature of 35℃. The eluent comprises water with a temperature of 95ºC. The main part of the sucrose in the feed ends up in the extract flow. Furthermore the extract is depleted from non-sucrose and the main part of the impurities ends up in the raffinate. Process calculations showed that the purity of the sugar liquor can be increased from about 90% to more than 99% with respect to the sucrose content. The raffinate typically contained less than 1% of the sugar in the feed (sucrose concentration 0.1%).

Figure 4 SMB-pilot at CSM (1: eluent, 2: raw juice (cooled), 3: HPLC-pumps, 4: oilbath for heating, 5: SMB carrousel, 6: additional external heating of columns, 7: collection of extract, raffinate & recycle, 8: PC & data-acquisition).

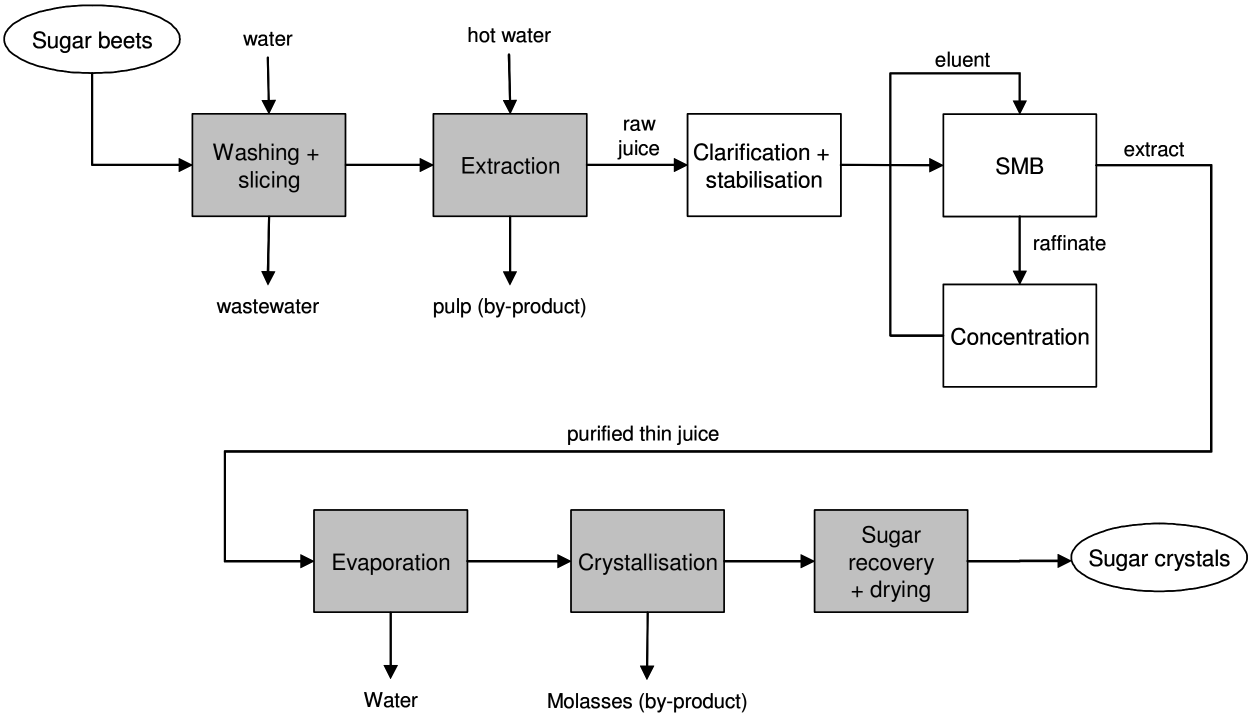

Figure 5 New developed process for the production of sucrose from sugar beets.

Increasing the adsorbent's surface temperature is done by bringing the eluent at a high temperature. At this high temperature the sugar, which was bound by the adsorbent at low temperature, will desorb, resulting in a raise of the sugar concentration in the liquor. After desorption, the sugar juice can be concentrated further and crystallized with similar techniques as applied in the conventional process. However, due to the reduced impurities content the crystallisation is more efficient with respect to the number of crystallisation steps, sugar yield and the amount of molasses produced.

A process model model was used to calculate the size, the flows and the performance of the SMB unit. The quality of the thin juice (purity and sugar concentration), the sugar losses to waste streams and the capacity of the installation are strongly interconnected and strongly depend on the process conditions chosen. For example optimalisation of the purity shall results in a lower sugar concentration and larger losses to the waste streams. Therefore an optimalisation algorithm was designed to minimize costs and taking into account:

- the effect of a higher purity of the thin juice on the crystallisation yield and thereby on the overall sugar yield;
- the impact of sugar concentration on the energy use in the evaporator;
- the value of sugar in the waste streams.

Model calculations identified the most important design parameters of the SMB unit. On basis of knowledge of the relationship between particle porosity, adsorption capacity and the SMB volume, the unit was resized. Initially the bed volume of the SMB unit for a plant with a capacity of 450 m^3 raw juice per hour was designed to be 3,000 m^3 which would be unacceptably large. However, using the optimization routine the size of the installation could be reduced considerably to 150 m^3 (factor 20) and thereby reducing the costs for the adsorption unit.

SMB pilot experiments were carried-out on pilot scale at the production site of a Dutch sugar company (CSM) during the campaign of 2005 (see figure 4). These pilot experiments showed that a temperature swing can be realised and sustained in an SMB installation. Modifications of the installation consisted of double-walled columns in combination with air heaters and heating-up the eluent stream. Unfortunately no good separation and concentration of the sugar was obtained due to settling down of the bed, which resulted in a dead volume of 13%. The hands-on experience gained sofar will be used in new experiments in the sugar campaign of 2006.

Conclusions

An improved method is proposed for refining raw juice from sugar beets (or any other liquor containing mono, di or trisaccharides). Key element is the use of an SMB-unit in which the juice is contacted with an adsorbent which is fit or adapted to accumulate sucrose on its surface. The adsorbent is capable to exhibit CH-π interactions and/or hydrogen bonding interactions. To accumulate sucrose, the juice is contacted with the adsorbent's surface at a low temperature, while, to collect sucrose, the adsorbent's surface is washed out by an eluent at an elevated temperature. Experiments showed that applying such a temperature swing also contributes to a microbial stable process and overcomes pressure build up.

Calculations, using an experimentally validated process model, provided insight into the possibilities of Amberchrom to obtain a separation and concentration increase using a temperature swing. It was concluded that, from a technical perspective, Amberchrom is a suitable adsorbent. From an economical perspective, however, the costs have to be reduced. The material, of which Amberchrom is made of, is not expensive and therefore important progress can be made when the present adsorbent production capacity is scaled up to the level required for the new sugar process. In addition further process development is taking place and a research programme is carried out to increase the capacity of the adsorbent. The process model is used to elucidate the effect of particle porosity, adsorption capacity and particle size on the size of the SMB unit.

Acknowledgements

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